

STIC Search Report

Biotech-Chem Library

STIC Database Tracking Number: 161714

TO: Ben Sackey
Location: 5b31 / 5c18
Art Unit: 1626
Tuesday, August 23, 2005

Case Serial Number: 10/631268

From: Noble Jarrell
Location: Biotech-Chem Library
Rem 1B71
Phone: 272-2556

Noble.jarrell@uspto.gov

Search Notes

Access DB# 161714

SEARCH REQUEST FORM

Scientific and Technical Information Center

Requester's Full Name: BEN SACKCY Examiner #: 73489 Date: 8/6/05
 Art Unit: 1626 Phone Number 302-0704 Serial Number: 10/631,268
 Mail Box and Bldg/Room Location: REM 5B3/Results Format Preferred (circle): PAPER DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

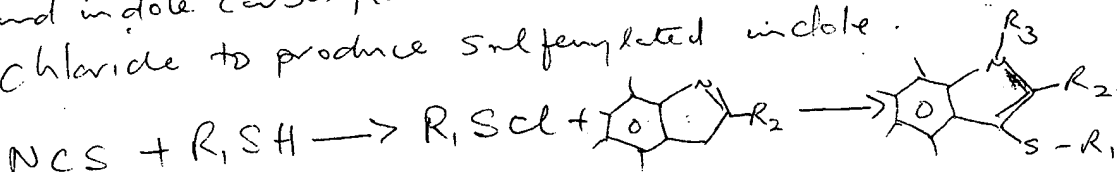
 Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc, if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: 3-Sulfenylated indole-2-Carboxylates
 Inventors (please provide full names): Hamilton et al.

Earliest Priority Filing Date: 7/31/02

For Sequence Searches Only Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

A one-step method of sulfenylation of 2-Carboxyindoles comprising mixing N-chlorosuccinimide and R₁SH, combining and indole carboxylate with a mixture containing Sulfenyl chloride to produce sulfenylated indole.



Thanks

STAFF USE ONLY

Type of Search

Vendors and cost where applicable

Searcher: noble NA Sequence (#) _____ STN _____
 Searcher Phone #: _____ AA Sequence (#) _____ Dialog _____
 Searcher Location: _____ Structure (#) 4 Questel/Orbit _____
 Date Searcher Picked Up: _____ Bibliographic ✓ Dr.Link _____
 Date Completed: 8/23/05 Litigation _____ Lexis/Nexis _____
 Searcher Prep & Review Time: 53/10 Fulltext _____ Sequence Systems _____
 Clerical Prep Time: _____ Patent Family _____ WWW/Internet _____
 Online Time: 53 Other _____ Other (specify) _____

=> d his

(FILE 'HOME' ENTERED AT 09:40:45 ON 23 AUG 2005)

FILE 'HCAPLUS' ENTERED AT 09:40:51 ON 23 AUG 2005

L1 1 US2004133014/PN OR (US2003-631268# OR US2002-400092#)/AP,PRN

FILE 'REGISTRY' ENTERED AT 09:41:42 ON 23 AUG 2005

FILE 'HCAPLUS' ENTERED AT 09:41:42 ON 23 AUG 2005

L2 TRA L1 1- RN : 42 TERMS

FILE 'REGISTRY' ENTERED AT 09:41:43 ON 23 AUG 2005

L3 42 SEA L2

FILE 'WPIX' ENTERED AT 09:41:48 ON 23 AUG 2005

L4 1 L1

=> b hcap

FILE 'HCAPLUS' ENTERED AT 09:42:09 ON 23 AUG 2005

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

COPYRIGHT (C) 2005 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December 26, 1996), unless otherwise indicated in the original publications. The CA Lexicon is the copyrighted intellectual property of the the American Chemical Society and is provided to assist you in searching databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS.1907 - 23 Aug 2005 VOL 143 ISS 9

FILE LAST UPDATED: 22 Aug 2005 (20050822/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> d all l1 tot

L1 ANSWER 1 OF 1 HCAPLUS COPYRIGHT 2005 ACS on STN

AN 2004:550803 HCAPLUS

DN 141:106369

ED Entered STN: 09 Jul 2004

TI Method for 3-sulfenylation of indole-2-carboxylates by chlorination of thiols to sulfenyl chlorides

IN Wall Hamilton, Harriet; Krasutsky, Alexei P.; Reed, Jessica; Schlosser, Kevin

PA USA

SO U.S. Pat. Appl. Publ., 13 pp.

CODEN: USXXCO

DT Patent

LA English

IC ICM C07D209-36

INCL 548484000

CC 27-11 (Heterocyclic Compounds (One Hetero Atom))

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2004133014	A1	20040708	US 2003-631268	20030731 <--
PRAI	US 2002-400092P	P	20020731	<--	

Search done by ~~Boon Saline~~

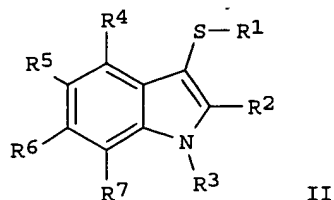
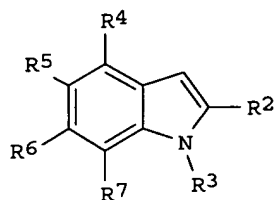
Noble Jarrell

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
US 2004133014	ICM	C07D209-36
	INCL	548484000
US 2004133014	NCL	548/484.000
	ECLA	C07D209/42; C07D513/04+281B+209B

OS CASREACT 141:106369; MARPAT 141:106369 <--

GI



- AB A highly efficient one-pot procedure for 3-sulfenylation of indole 2-carboxylates is described. Treatment of thiols of formula HSR1 [R1 = C1-6 alkyl, C2-6 alkoxy carbonyl, C3-7 cycloalkyl, C3-7 heterocycloalkyl, C1-6 alkyl-S(O)mRa, -C1-6 alkyl-S(O)mNRbRc, C1-6 alkyl-NRbRc, or C1-6 alkyl-CO-NRbRc, aryl, heteroaryl, etc.; m = 1, 2; Ra, Rb, Rc = H, C1-6 alkyl, C3-7 cycloalkyl, C3-6 heterocycloalkyl, or aryl] with N-chlorosuccinimide at -78° in CH₂Cl₂ affords sulfenyl chlorides of formula R1SCl in situ that readily react with indole 2-carboxylates [I; R2 = CO₂H, tetrazolyl, C2-6 alkoxy carbonyl, CONRbRc (Rb, Rc = H, C1-6 alkyl), S(O)mRa, or -S(O)mNRbRc, NRbRc, etc. (wherein m = 1, 2; Ra, Rb, Rc = H, C1-6 alkyl, C3-7 cycloalkyl, C3-6 heterocycloalkyl, or aryl); R3 = H, each optionally substituted alkyl C1-6 or C1-6 alkanoyl; R4-R7 = H, halo, C1-6 alkyl, C1-6 alkoxy, cyano, C3-7 cycloalkyl, C3-7 heterocycloalkyl, C1-6 alkyl-S(O)mRa, -C1-6 -S(O)mNRbRc, C1-6 alkyl-NRbRc, or C1-6 alkyl-CO-NRbRc, C1-6 alkyl-COR1, S(O)mRa, S(O)mNRbRc, NRbRc, CONRbRc, aryl, heteroaryl, etc. (wherein m = 1, 2; Ra, Rb, Rc = H, C1-6 alkyl, C3-7 cycloalkyl, C3-6 heterocycloalkyl, heteroaryl or aryl)] to give 3-thioindoles (II) in high yields. This new method is milder, produces less waste, and is compatible with a wide range of thiol and indole functionality. It is also used for intramol. sulfenylation of N-(2-mercaptoethyl)-1H-indolecarboxamide derivs. to form a indole-fused 1,4-thiazepane ring. Thus, to a cooled solution of N-chlorosuccinimide (2.74 g, 20.6 mmol) in CH₂Cl₂ (125 mL) at -78°, 3-methoxythiophenol (2.55 mL, 20.6 mmol) was added. The reaction was warmed to 0° over 15 min and a solution of indole-2-carboxylic acid Me ester (3 g, 17.1 mmol) in CH₂Cl₂ (25 mL) was added. The reaction stirred at 0° for 1 h, then concentrated under reduced pressure and the residue was suspended in H₂O and stirred for 30 min to give, after filtration of the solid and recrystn. from EtOAc/hexanes to give 3-[(3-methoxyphenyl)thio]-1H-indole-2-carboxylic acid Me ester (3.22 g, 60%).
- ST phenylthioindolecarboxylate alkylthioindolecarboxylate prepn; chlorosuccinimide chlorination thiol; thiol chlorination sulfenylation indolecarboxylate; sulfenyl chloride prepn sulfenylation indolecarboxylate; intramol sulfenylation mercaptoethylindolecarboxamide indolothiazepane prepn
- IT Chlorination
(3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)
- IT Thiols, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)
- IT Cyclization
(intramol. sulfenylation of N-(2-mercaptoethyl)indolecarboxamide

derivs. to indole-fused 1,4-thiaazacycloheptane ring; 3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT Sulfenyl compounds

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(sulfenyl chlorides; 3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT Substitution reaction

(sulfenylation; 3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT 60-23-1, 2-Aminoethanethiol 75-66-1, tert-Butyl mercaptan 100-53-8, Benzyl mercaptan 106-45-6, 4-Methylthiophenol 106-53-6, 4-Bromothiophenol 108-40-7, 3-Methylthiophenol 108-98-5, Thiophenol, reactions 128-09-6, N-Chlorosuccinimide 348-36-7, 5-Fluoro-1H-indole-2-carboxylic acid ethyl ester 1202-04-6, 1H-Indole-2-carboxylic acid methyl ester 2935-90-2, 3-Mercaptopropanoic acid methyl ester 3770-50-1, 1H-Indole-2-carboxylic acid ethyl ester 4382-54-1, 5-Methoxy-1H-indole-2-carboxylic acid 6320-01-0, 3-Bromothiophenol 7217-59-6, 2-Methoxythiophenol 7684-18-6, 3-Amino-2-methylpropane-2-thiol 15570-12-4, 3-Methoxythiophenol 17481-19-5, 3-Chloropropanethiol 67385-09-5, 2-(tert-Butoxycarbonylamino)ethanethiol 67929-86-6, 5-Methoxy-1H-indole-2-carboxylic acid methyl ester 67929-87-7, 5-Methoxy-1-methyl-1H-indole-2-carboxylic acid methyl ester 130445-25-9, 5-Methoxy-1-methyl-1H-indole-2-carboxamide

RL: RCT (Reactant); RACT (Reactant or reagent)

(3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT 671783-58-7P, N-(2-Mercaptoethyl)5-methoxy-1H-indole-2-carboxamide
671783-60-1P, N-(2-Mercapto-2-methylpropyl)5-methoxy-1H-indole-2-carboxamide

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT 671783-29-2P, 5-Methoxy-1-methyl-3-[(3-chloropropyl)thio]-1H-indole-2-carboxylic acid methyl ester 671783-31-6P, 5-Methoxy-1-methyl-3-(phenylthio)-1H-indole-2-carboxylic acid methyl ester 671783-33-8P, 5-Methoxy-1-methyl-3-[(4-methylphenyl)thio]-1H-indole-2-carboxamide 671783-35-0P, 3-(Benzylthio)-5-methoxy-1-methyl-1H-indole-2-carboxamide 671783-42-9P, 5-Methoxy-3-[[2-(methoxycarbonyl)ethyl]thio]-1H-indole-2-carboxylic acid methyl ester 671783-44-1P, 5-Methoxy-3-[[2-(tert-butoxycarbonylamino)ethyl]thio]-1H-indole-2-carboxylic acid methyl ester 671783-46-3P, 3-[(3-Methylphenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 671783-48-5P, 3-[(3-Methoxyphenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 671783-50-9P, 3-[(3-Bromophenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 671783-62-3P 671783-64-5P 718614-74-5P, 3-[(4-Bromophenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 718614-75-6P, 3-[(2-Methoxyphenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 718614-76-7P, 3-[(3-Methoxyphenyl)thio]-1H-indole-2-carboxylic acid methyl ester 718614-77-8P, 3-[(4-Bromophenyl)thio]-1H-indole-2-carboxylic acid methyl ester 718614-78-9P, 3-[(3-Methylphenyl)thio]-1H-indole-2-carboxylic acid methyl ester

RL: SPN (Synthetic preparation); PREP (Preparation)

(3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT 718614-72-3P, 5-Methoxy-1-methyl-3-(tert-butylthio)-1H-indole-2-carboxylic acid methyl ester 718614-73-4P, 5-Methoxy-1-methyl-3-(tert-butylthio)-1H-indole-2-carboxamide

RL: SPN (Synthetic preparation); PREP (Preparation)

(failed reaction; 3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

=> b wpix

FILE 'WPIX' ENTERED AT 09:42:16 ON 23 AUG 2005

COPYRIGHT (C) 2005 THE THOMSON CORPORATION

FILE LAST UPDATED: 18 AUG 2005 <20050818/UP>
 MOST RECENT DERWENT UPDATE: 200553 <200553/DW>
 DERWENT WORLD PATENTS INDEX SUBSCRIBER FILE, COVERS 1963 TO DATE

>>> FOR A COPY OF THE DERWENT WORLD PATENTS INDEX STN USER GUIDE,
 PLEASE VISIT:
http://www.stn-international.de/training_center/patents/stn_guide.pdf <<<

>>> FOR DETAILS OF THE PATENTS COVERED IN CURRENT UPDATES, SEE
<http://thomsonderwent.com/coverage/latestupdates/> <<<

>>> FOR INFORMATION ON ALL DERWENT WORLD PATENTS INDEX USER
 GUIDES, PLEASE VISIT:
<http://thomsonderwent.com/support/userguides/> <<<

>>> NEW! FAST-ALERTING ACCESS TO NEWLY-PUBLISHED PATENT
 DOCUMENTATION NOW AVAILABLE IN DERWENT WORLD PATENTS INDEX
 FIRST VIEW - FILE WPIFV.
 FOR FURTHER DETAILS: <http://www.thomsonderwent.com/dwpifv> <<<

>>> THE CPI AND EPI MANUAL CODES HAVE BEEN REVISED FROM UPDATE 200501.
 PLEASE CHECK:
<http://thomsonderwent.com/support/dwpieref/reftools/classification/code-revision/>
 FOR DETAILS. <<<
 'BIX BI,ABEX' IS DEFAULT SEARCH FIELD FOR 'WPIX' FILE

=> d all 14 tot

L4 ANSWER 1 OF 1 WPIX COPYRIGHT 2005 THE THOMSON CORP on STN
 AN 2004-524924 [50] WPIX
 DNC C2004-193108
 TI Preparation of 3-thioindole-2-carboxylate derivatives useful in treatment
 of e.g. HIV, obesity involves sulfenylation of 2-carboxy-indole
 derivatives with in situ generated sulfenyl chloride.
 DC B02
 IN KRASUTSKY, A P; REED, J; SCHLOSSER, K; WALL HAMILTON, H
 PA (KRAS-I) KRASUTSKY A P; (REED-I) REED J; (SCHL-I) SCHLOSSER K; (HAMI-I)
 WALL HAMILTON H
 CYC 1
 PI US 2004133014 A1 20040708 (200450)* 13 C07D209-36 <--
 ADT US 2004133014 A1 Provisional US 2002-400092P 20020731, US
 2003-631268 20030731
 PRAI US 2002-400092P 20020731; US 2003-631268
 20030731
 IC ICM C07D209-36
 AB US2004133014 A UPAB: 20040805
 NOVELTY - Sulfenylation of 2-carboxy-indole derivatives involves reacting
 N-chlorosuccinimide with thiols to generate sulfenyl chloride, which is
 reacted with indole-2-carboxylate derivatives to give 3-sulfenylated-2-
 carboxy-indole derivatives.
 DETAILED DESCRIPTION - Sulfenylation (M1) of 2-carboxy-indole
 derivatives of formula (I) involves (a) mixing N-chlorosuccinimide with
 thiol in a liquid (L1) to form sulfenyl chloride of formula R1SCl as a
 homogeneous or heterogeneous mixture and (b) combining the in situ
 generated sulfenyl chloride with (I) to give 3-sulfenylated indole
 derivatives of formula (II).
 R1 = 1-6C alkyl, 3-7C (hetero)cycloalkyl (all optionally partially
 unsaturated and substituted by T1 or aryl(1-6C)alkoxy), (hetero)aryl
 (optionally substituted by T1 and aryl(1-6C)alkoxy), 2-6C alkoxy carbonyl,
 (1-6C)-S(O)mRa, -(1-6C)-S(O)mNRbRc, (1-6C)-NRbRc or (1-6C)-C(=O)-NRbRc;
 T1 = T2, aryl carbonyl, 1-6C alkoxy, 1-6C alkanoyl, 1-6C
 alkoxy carbonyl, 1-6C alkanoyloxy, -S(O)mRa, -S(O)mNRbRc, NRbRc or
 -C(=O)NRbRc;

Search done by Ross Schipe

T2 = (hetero)aryl, (hetero)aryloxy, hydroxy, nitro, halo or cyano;
m = 1 or 2;
Ra, Rb, and Rc = H, 1-6C alkyl, 3-7C (hetero)cycloalkyl or aryl;
R2 = carboxy, tetrazolyl, 2-6C alkoxy carbonyl, -C(O)NRb'Rc',
-S(O)mRa, -S(O)mNRb'Rc', NRb'Rc' or -C(=O)Rd (optionally substituted
by T2);
Rb' and Rc' = H or 1-6C alkyl;
R3 = H, 1-6C alkyl or 1-6C alkanoyl (optionally substituted by T2);
R4 - R7 = 1-6C alkyl, 3-7C (hetero)cycloalkyl (all optionally
partially unsaturated and substituted by T1) or (hetero)aryl (optionally
substituted by T1), H, halo, 1-6C alkoxy, cyano, (1-6C)-S(O)mRa,
-(1-6C)-S(O)mNRb'Rc', (1-6C)-NRb'Rc', (1-6C)-C(=O)-NRb'Rc',
(1-6C)-C(=O)R1, S(O)mRa', S(O)mNRb'Rc', NRb'Rc', C(=O)-NRb'Rc' or C(=O)Rd;
Ra', Rb' and Rc' = Ra or heteroaryl.
Provided that not all of R4 - R7 are H.
NB: Rd not defined.
An INDEPENDENT CLAIM is included for intramolecular sulfenylation
(M2) of 2-carboxyindoles involving mixing N-chlorosuccinimide with a thiol
of formula (III) in liquid (L1) to generate sulfenyl chloride of formula
(IV) followed by intramolecular sulfenylation of (IV) to give sulfenylated
indole derivative of formula (V).
R8 and R9 = H or 1-6C alkyl (optionally substituted by T2);
n = 0 - 4;
X = CR7R8, O or NRb' where Rb' = H, acyl or 1-6C alkyl (optionally
substituted with T2).

ACTIVITY - Anti-HIV; Anorectic; Antiallergic.

MECHANISM OF ACTION - Endothelial antagonist.

USE - For the preparation of 3-thioindole-2-carboxylates (claimed),
which are useful as endothelin antagonists, anti-allergy agents and also
in the treatment of HIV and obesity.

ADVANTAGE - The method is one step and includes milder conditions
than those associated with the use of corrosive chlorine or sulfur
chloride, as well as fast reaction times, easy work-up and improved
yields. The in-situ formation method using N-chlorosuccinimide enhances
the scope of the reaction, previously limited by the stability and ease of
isolation of sulfenyl chlorides, avoids the formation of one equivalent of
wasted thiol that occurs when a disulfide is used as the electrophilic
sulfur source and possesses greater flexibility than other reported
methods because the indole nitrogen does not require protection.

Dwg.0/0

FS CPI

FA AB; GI; DCN

MC CPI: B06-H; B14-A02B1; B14-E12; B14-G02A; B14-L06

=> b home

FILE 'HOME' ENTERED AT 09:42:20 ON 23 AUG 2005

=>

=> b reg

FILE 'REGISTRY' ENTERED AT 10:09:49 ON 23 AUG 2005

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

COPYRIGHT (C) 2005 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 22 AUG 2005 HIGHEST RN 861291-85-2

DICTIONARY FILE UPDATES: 22 AUG 2005 HIGHEST RN 861291-85-2

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 18, 2005

Please note that search-term pricing does apply when conducting SmartSELECT searches.

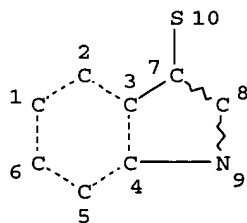
```
*****
*
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
*
*****
```

Structure search iteration limits have been increased. See HELP SLIMITS for details.

Experimental and calculated property data are now available. For more information enter HELP PROP at an arrow prompt in the file or refer to the file summary sheet on the web at:
<http://www.cas.org/ONLINE/DBSS/registryss.html>

=> d que sta l27

L25 STR



NODE ATTRIBUTES:

CONNECT IS E3 RC AT 8

CONNECT IS M2 RC AT 10

DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED

NUMBER OF NODES IS 10

STEREO ATTRIBUTES: NONE

L27 4263 SEA FILE=REGISTRY SSS FUL L25

100.0% PROCESSED 11225 ITERATIONS

4263 ANSWERS

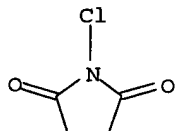
SEARCH TIME: 00.00.01

Search done by ~~Reese G. H. H. H.~~

Noble Jarrell

=> d ide l44 tot

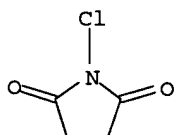
L44 ANSWER 1 OF 9 REGISTRY COPYRIGHT 2005 ACS on STN
RN 815597-82-1 REGISTRY
ED Entered STN: 18 Jan 2005
CN 2,5-Pyrrolidinedione, 1-chloro-, conjugate monoacid (9CI) (CA INDEX NAME)
MF C4 H4 Cl N O2 . H
SR CA
LC STN Files: CA, CAPLUS
CRN (128-09-6)



● H⁺

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

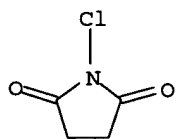
L44 ANSWER 2 OF 9 REGISTRY COPYRIGHT 2005 ACS on STN
RN 815597-81-0 REGISTRY
ED Entered STN: 18 Jan 2005
CN 2,5-Pyrrolidinedione, 1-chloro-, conjugate triacid (9CI) (CA INDEX NAME)
MF C4 H4 Cl N O2 . 3 H
SR CA
LC STN Files: CA, CAPLUS
CRN (128-09-6)



●3 H⁺

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

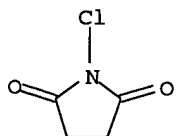
L44 ANSWER 3 OF 9 REGISTRY COPYRIGHT 2005 ACS on STN
RN 815597-79-6 REGISTRY
ED Entered STN: 18 Jan 2005
CN 2,5-Pyrrolidinedione, 1-chloro-, conjugate diacid (9CI) (CA INDEX NAME)
MF C4 H4 Cl N O2 . 2 H
SR CA
LC STN Files: CA, CAPLUS
CRN (128-09-6)



● 2 H⁺

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L44 ANSWER 4 OF 9 REGISTRY COPYRIGHT 2005 ACS on STN
RN 90685-90-8 REGISTRY
ED Entered STN: 16 Nov 1984
CN 2,5-Pyrrolidinedione, 1-chloro-, monoammoniate (9CI) (CA INDEX NAME)
MF C4 H4 Cl N O2 . H3 N
LC STN Files: CA, CAPLUS
CRN (128-09-6)



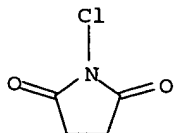
● NH₃

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L44 ANSWER 5 OF 9 REGISTRY COPYRIGHT 2005 ACS on STN
RN 90124-80-4 REGISTRY
ED Entered STN: 16 Nov 1984
CN 2,5-Pyrrolidinedione, 1-chloro-, compd. with thiobis[methane] (1:1) (9CI)
(CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Methane, thiobis-, compd. with 1-chloro-2,5-pyrrolidinedione (1:1) (9CI)
MF C4 H4 Cl N O2 . C2 H6 S
LC STN Files: BEILSTEIN*, CA, CAPLUS, CASREACT
(*File contains numerically searchable property data)

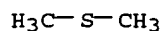
CM 1

CRN 128-09-6
CMF C4 H4 Cl N O2



CM 2

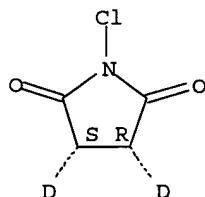
CRN 75-18-3
CMF C2 H6 S



1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L44 ANSWER 6 OF 9 REGISTRY COPYRIGHT 2005 ACS on STN
RN 66996-79-0 REGISTRY
ED Entered STN: 16 Nov 1984
CN 2,5-Pyrrolidinedione-3,4-d2, 1-chloro-, cis- (9CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C4 H2 Cl D2 N O2
LC STN Files: CA, CAPLUS

Relative stereochemistry.

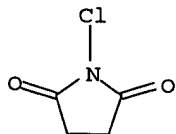


2 REFERENCES IN FILE CA (1907 TO DATE)
2 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L44 ANSWER 7 OF 9 REGISTRY COPYRIGHT 2005 ACS on STN
RN 54437-73-9 REGISTRY
ED Entered STN: 16 Nov 1984
CN 2,5-Pyrrolidinedione, 1-chloro-, compd. with N,N-diethylethanamine (1:1)
(9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Ethanamine, N,N-diethyl-, compd. with 1-chloro-2,5-pyrrolidinedione (1:1)
MF C6 H15 N . C4 H4 Cl N O2
LC STN Files: CA, CAPLUS

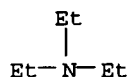
CM 1

CRN 128-09-6
CMF C4 H4 Cl N O2



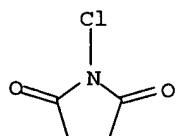
CM 2

CRN 121-44-8
CMF C6 H15 N



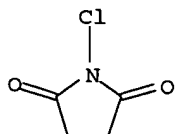
1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L44 ANSWER 8 OF 9 REGISTRY COPYRIGHT 2005 ACS on STN
RN 38144-43-3 REGISTRY
ED Entered STN: 16 Nov 1984
CN 2,5-Pyrrolidinedione, 1-chloro-, radical ion(1-) (9CI) (CA INDEX NAME)
OTHER NAMES:
CN N-Chlorosuccinimide anion radical
MF C4 H4 Cl N O2
CI RIS
LC STN Files: CA, CAPLUS



5 REFERENCES IN FILE CA (1907 TO DATE)
5 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L44 ANSWER 9 OF 9 REGISTRY COPYRIGHT 2005 ACS on STN
RN 128-09-6 REGISTRY
ED Entered STN: 16 Nov 1984
CN 2,5-Pyrrolidinedione, 1-chloro- (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Succinimide, N-chloro- (6CI, 7CI, 8CI)
OTHER NAMES:
CN 1-Chloro-2,5-pyrrolidinedione
CN Chlorosuccinimide
CN N-Chlorosuccinimide
CN NSC 8748
CN Succinchlorimide
CN Succinic N-chloroimide
FS 3D CONCORD
MF C4 H4 Cl N O2
CI COM
LC STN Files: AGRICOLA, ANABSTR, BEILSTEIN*, BIOBUSINESS, BIOSIS, CA, CANCERLIT, CAOLD, CAPLUS, CASREACT, CBNB, CEN, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSCHM, DETHERM*, EMBASE, GMELIN*, HODOC*, HSDB*, IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, MRCK*, MSDS-OHS, PIRA, PROMT, PS, RTECS*, SPECINFO, SYNTHLINE, TOXCENTER, USAN, USPAT2, USPATFULL
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1261 REFERENCES IN FILE CA (1907 TO DATE)
 14 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
 1272 REFERENCES IN FILE CAPLUS (1907 TO DATE)
 41 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

=> d his

(FILE 'HOME' ENTERED AT 09:40:45 ON 23 AUG 2005)

FILE 'HCAPLUS' ENTERED AT 09:40:51 ON 23 AUG 2005

L1 1 US2004133014/PN OR (US2003-631268# OR US2002-400092#)/AP, PRN

FILE 'REGISTRY' ENTERED AT 09:41:42 ON 23 AUG 2005

FILE 'HCAPLUS' ENTERED AT 09:41:42 ON 23 AUG 2005

L2 TRA L1 1- RN : 42 TERMS

FILE 'REGISTRY' ENTERED AT 09:41:43 ON 23 AUG 2005

L3 42 SEA L2

FILE 'WPIX' ENTERED AT 09:41:48 ON 23 AUG 2005

L4 1 L1

FILE 'HCAPLUS' ENTERED AT 09:50:40 ON 23 AUG 2005

E WALL/AU

E WALL H/AU

L5 7 E3

E WALL HAMILTON/AU

L6 1 E4

E HAMILTON H/AU

L7 28 E3-4, E23

E HAMILTON HARRIET/AU

L8 46 E3-6

E KRASUTSKY A/AU

L9 9 E4-6

E REED J/AU

L10 72 E3-4

E REED JESS/AU

L11 56 E3-9

E SCHLOSSER K/AU

L12 15 E3, E8-9

E WRANER/CS, PA

E WARNNER/CS, PA

E WARNER/CS, PA

L13 7002 E3-4

E WARNERLAMB/CS, PA

L14 5 E5-7

E WARNER LAMB/CS, PA

L15 5749 WARNER LAMB?/CS, PA

E SUBSTITUTION REAC/CT

E E4+ALL

L16 309 SUBSTITUTION REACTION+OLD, NT/CT (L) (SULFEN? OR SULPHEN?)

E SULFENYL COMPOUNDS/CT

E E3+ALL

L17 9296 SULFENYL COMPOUNDS+NT/CT

L18 937 L17 (L) (?FLUORIDE? OR ?CHLORIDE? OR ?BROMID? OR ?IODID? OR ?HA

L19 3 L18 (L) PREP+NT/RL AND L16

L20 1 L19 AND L5-15

L21 2 L19 NOT L20

L22 QUE PY<=2002 OR AY<=2002 OR PRY<=2002 OR PD<20020731 OR AD<2002

L23 2 L21 AND L22

L24 2 L21, L23

FILE 'REGISTRY' ENTERED AT 10:00:02 ON 23 AUG 2005

L25 STR

Search done by Ross Schipe

L26 50 L25
L27 4263 L25 FULL

FILE 'HCAPLUS' ENTERED AT 10:01:59 ON 23 AUG 2005

L28 820 L27
L29 515 L28 (L) PREP+NT/RL
L30 51 L17 AND L16
L31 1 L30 AND L5-15
L32 50 L30 NOT L31
E THIOL/CT
E THIOLS/CT
E E3+ALL
E E2
E E3+ALL
L33 QUE "THIOLS (ORGANIC)"+OLD,NT/CT
L34 6 L33 AND L32
L35 11 ?THIOL? AND L32
L36 11 L34,L35
L37 42909 L33 (L) RACT+NT/RL
L38 37627 ?THIOL? (L) RACT+NT/RL
L39 9 L37,L38 AND L36
L40 11 L36,L39

FILE 'REGISTRY' ENTERED AT 10:05:41 ON 23 AUG 2005

L41 1 128-09-6
L42 22 C4H4CLNO2 AND NC4/ES
L43 14 L42 NOT (MXS/CI OR MIXT)
SEL RN 1-3 7-9 11 13-14 L43
L44 9 E1-9 AND L43
L45 5 L43 NOT L44
L46 8 L42 NOT L43
L47 13 L45,L46

FILE 'HCAPLUS' ENTERED AT 10:10:30 ON 23 AUG 2005

L48 1276 L44
L49 2654 2(1A)5(1A) (PYRROLIDINEDIONE? OR PYRROLIDIN?(1A)DIONE?) (4A)CHLO
L50 1117 L48,L49(L) RACT+NT/RL
L51 1 L20,L31 AND L50
L52 1 L20,L31,L51
L53 0 L24,L40 AND L48-50
L54 12 L24,L40

FILE 'CASREACT' ENTERED AT 10:17:15 ON 23 AUG 2005

L55 STR
L56 0 L55
L57 12 L55 FULL
E HAILTON H/AU
E HAMILTON H/AU
L58 16 E5-7
E HAMILTON WALL/AU
E KRASULSKY A/AU
E SCHLOSSER K/AU
L59 2 E4-5
E REED J/AU
L60 19 E3-7,E10-11
L61 644 (WARNERLAMB? OR WARNER LAMB?)/CS,PA
L62 0 L57 AND L58-61
L63 31 L58-61 AND ?THIOL?
L64 4 L58-60 AND ?THIOL?
SEL AN 1-2 L64
L65 2 E1-2 AND L64
L66 11 L57 AND L22
L67 12 L57,L66
L68 3 L63 AND SULFEN?
SEL AN 2-3 5-12 L57
L69 10 E3-12 AND L57 AND L67

```

L70      STR
L71      0 L70
L72      7 L70 FULL
L73      0 L72 AND L58-61
L74      7 L72 AND L22
L75      7 L72,L74
L76      0 L69 AND L75
L77      17 L69,L75
L78      3 L65,L68

```

=> b hcap

FILE 'HCAPLUS' ENTERED AT 10:39:42 ON 23 AUG 2005
 USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
 PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
 COPYRIGHT (C) 2005 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December 26, 1996), unless otherwise indicated in the original publications. The CA Lexicon is the copyrighted intellectual property of the the American Chemical Society and is provided to assist you in searching databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS 1907 - 23 Aug 2005 VOL 143 ISS 9
 FILE LAST UPDATED: 22 Aug 2005 (20050822/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> d all fhitrstr 152 tot

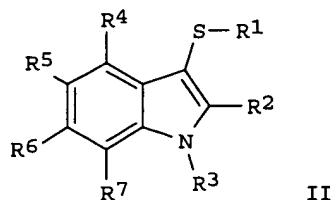
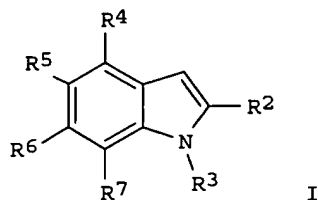
```

L52  ANSWER 1 OF 1  HCAPLUS  COPYRIGHT 2005 ACS on STN
AN   2004:550803  HCAPLUS
DN   141:106369
ED   Entered STN:  09 Jul 2004
TI   Method for 3-sulfenylation of indole-2-carboxylates by chlorination of
      thiols to sulfenyl chlorides
IN   Wall Hamilton, Harriet; Krasutsky, Alexei P.;
      Reed, Jessica; Schlosser, Kevin
PA   USA
SO   U.S. Pat. Appl. Publ., 13 pp.
      CODEN: USXXCO
DT   Patent
LA   English
IC   ICM  C07D209-36
INCL 548484000
CC   27-11 (Heterocyclic Compounds (One Hetero Atom))
FAN.CNT 1
      PATENT NO.          KIND   DATE          APPLICATION NO.          DATE
      -----
PI   US 2004133014      A1     20040708      US 2003-631268          20030731
PRAI US 2002-400092P    P       20020731
CLASS
      PATENT NO.          CLASS  PATENT FAMILY CLASSIFICATION CODES
      -----
US 2004133014          ICM     C07D209-36
                        INCL     548484000
US 2004133014          NCL     548/484.000
                        ECLA     C07D209/42; C07D513/04+281B+209B
OS   CASREACT 141:106369; MARPAT 141:106369

```

Search done by Ross Schipe

GI



AB A highly efficient one-pot procedure for 3-sulfenylation of indole 2-carboxylates is described. Treatment of thiols of formula HSR1 [R1 = C1-6 alkyl, C2-6 alkoxy carbonyl, C3-7 cycloalkyl, C3-7 heterocycloalkyl, C1-6 alkyl-S(O)mRa, -C1-6 alkyl-S(O)mNRbRc, C1-6 alkyl-NRbRc, or C1-6 alkyl-CO-NRbRc, aryl, heteroaryl, etc.; m = 1, 2; Ra, Rb, Rc = H, C1-6 alkyl, C3-7 cycloalkyl, C3-6 heterocycloalkyl, or aryl] with N-chlorosuccinimide at -78° in CH2Cl2 affords sulfenyl chlorides of formula R1SCl in situ that readily react with indole 2-carboxylates [I; R2 = CO2H, tetrazolyl, C2-6 alkoxy carbonyl, CONRbRc (Rb, Rc = H, C1-6 alkyl), S(O)mRa, or -S(O)mNRbRc, NRbRc, etc. (wherein m = 1, 2; Ra, Rb, Rc = H, C1-6 alkyl, C3-7 cycloalkyl, C3-6 heterocycloalkyl, or aryl); R3 = H, each optionally substituted alkyl C1-6 or C1-6 alkanoyl; R4-R7 = H, halo, C1-6 alkyl, C1-6 alkoxy, cyano, C3-7 cycloalkyl, C3-7 heterocycloalkyl, C1-6 alkyl-S(O)mRa, -C1-6 -S(O)mNRbRc, C1-6 alkyl-NRbRc, or C1-6 alkyl-CO-NRbRc, C1-6 alkyl-COR1, S(O)mRa, S(O)mNRbRc, NRbRc, CONRbRc, aryl, heteroaryl, etc. (wherein m = 1, 2; Ra, Rb, Rc = H, C1-6 alkyl, C3-7 cycloalkyl, C3-6 heterocycloalkyl, heteroaryl or aryl)] to give 3-thioindoles (II) in high yields. This new method is milder, produces less waste, and is compatible with a wide range of thiol and indole functionality. It is also used for intramol. sulfenylation of N-(2-mercaptoethyl)-1H-indolecarboxamide derivs. to form an indole-fused 1,4-thiaazepane ring. Thus, to a cooled solution of N-chlorosuccinimide (2.74 g, 20.6 mmol) in CH2Cl2 (125 mL) at -78°, 3-methoxythiophenol (2.55 mL, 20.6 mmol) was added. The reaction was warmed to 0° over 15 min and a solution of indole-2-carboxylic acid Me ester (3 g, 17.1 mmol) in CH2Cl2 (25 mL) was added. The reaction stirred at 0° for 1 h, then concentrated under reduced pressure and the residue was suspended in H2O and stirred for 30 min to give, after filtration of the solid and recrystn. from EtOAc/hexanes to give 3-[(3-methoxyphenyl)thio]-1H-indole-2-carboxylic acid Me ester (3.22 g, 60%).

ST phenylthioindolecarboxylate alkylthioindolecarboxylate prepn;
chlorosuccinimide chlorination thiol; thiol chlorination sulfenylation
indolecarboxylate; sulfenyl chloride prepn sulfenylation
indolecarboxylate; intramol sulfenylation mercaptoethylindolecarboxamide
indolothiaazepane prepn

IT Chlorination
(3-sulfenylation of indole-2-carboxylates via in situ formation of
sulfenyl chlorides by chlorination of thiols)

IT Thiols, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(3-sulfenylation of indole-2-carboxylates via in situ formation of
sulfenyl chlorides by chlorination of thiols)

IT Cyclization
(intramol. sulfenylation of N-(2-mercaptoethyl)indolecarboxamide
derivs. to indole-fused 1,4-thiaazacycloheptane ring; 3-sulfenylation
of indole-2-carboxylates via in situ formation of sulfenyl chlorides by
chlorination of thiols)

IT Sulfenyl compounds
RL: RCT (Reactant); SPN (Synthetic preparation); PREP
(Preparation); RACT (Reactant or reagent)

(sulfenyl chlorides; 3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT Substitution reaction

(sulfenylation; 3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT 60-23-1, 2-Aminoethanethiol 75-66-1, tert-Butyl mercaptan 100-53-8, Benzyl mercaptan 106-45-6, 4-Methylthiophenol 106-53-6, 4-Bromothiophenol 108-40-7, 3-Methylthiophenol 108-98-5, Thiophenol, reactions 128-09-6, N-Chlorosuccinimide 348-36-7, 5-Fluoro-1H-indole-2-carboxylic acid ethyl ester 1202-04-6, 1H-Indole-2-carboxylic acid methyl ester 2935-90-2, 3-Mercaptopropanoic acid methyl ester 3770-50-1, 1H-Indole-2-carboxylic acid ethyl ester 4382-54-1, 5-Methoxy-1H-indole-2-carboxylic acid 6320-01-0, 3-Bromothiophenol 7217-59-6, 2-Methoxythiophenol 7684-18-6, 3-Amino-2-methylpropane-2-thiol 15570-12-4, 3-Methoxythiophenol 17481-19-5, 3-Chloropropanethiol 67385-09-5, 2-(tert-Butoxycarbonylamino)ethanethiol 67929-86-6, 5-Methoxy-1H-indole-2-carboxylic acid methyl ester 67929-87-7, 5-Methoxy-1-methyl-1H-indole-2-carboxylic acid methyl ester 130445-25-9, 5-Methoxy-1-methyl-1H-indole-2-carboxamide

RL: RCT (Reactant); RACT (Reactant or reagent)

(3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT 671783-58-7P, N-(2-Mercaptoethyl)5-methoxy-1H-indole-2-carboxamide 671783-60-1P, N-(2-Mercapto-2-methylpropyl)5-methoxy-1H-indole-2-carboxamide

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT 671783-29-2P, 5-Methoxy-1-methyl-3-[(3-chloropropyl)thio]-1H-indole-2-carboxylic acid methyl ester 671783-31-6P, 5-Methoxy-1-methyl-3-(phenylthio)-1H-indole-2-carboxylic acid methyl ester 671783-33-8P, 5-Methoxy-1-methyl-3-[(4-methylphenyl)thio]-1H-indole-2-carboxamide 671783-35-0P, 3-(Benzylthio)-5-methoxy-1-methyl-1H-indole-2-carboxamide 671783-42-9P, 5-Methoxy-3-[[2-(methoxycarbonyl)ethyl]thio]-1H-indole-2-carboxylic acid methyl ester 671783-44-1P, 5-Methoxy-3-[[2-(tert-butoxycarbonylamino)ethyl]thio]-1H-indole-2-carboxylic acid methyl ester 671783-46-3P, 3-[(3-Methylphenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 671783-48-5P, 3-[(3-Methoxyphenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 671783-50-9P, 3-[(3-Bromophenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 671783-62-3P 671783-64-5P 718614-74-5P, 3-[(4-Bromophenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 718614-75-6P, 3-[(2-Methoxyphenyl)thio]-1H-indole-2-carboxylic acid ethyl ester 718614-76-7P, 3-[(3-Methoxyphenyl)thio]-1H-indole-2-carboxylic acid methyl ester 718614-77-8P, 3-[(4-Bromophenyl)thio]-1H-indole-2-carboxylic acid methyl ester 718614-78-9P, 3-[(3-Methylphenyl)thio]-1H-indole-2-carboxylic acid methyl ester

RL: SPN (Synthetic preparation); PREP (Preparation)

(3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

IT 718614-72-3P, 5-Methoxy-1-methyl-3-(tert-butylthio)-1H-indole-2-carboxylic acid methyl ester 718614-73-4P, 5-Methoxy-1-methyl-3-(tert-butylthio)-1H-indole-2-carboxamide

RL: SPN (Synthetic preparation); PREP (Preparation)

(failed reaction; 3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

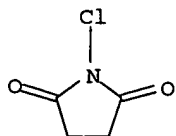
IT 128-09-6, N-Chlorosuccinimide

RL: RCT (Reactant); RACT (Reactant or reagent)

(3-sulfenylation of indole-2-carboxylates via in situ formation of sulfenyl chlorides by chlorination of thiols)

RN 128-09-6 HCAPLUS

CN 2,5-Pyrrolidinedione, 1-chloro- (9CI) (CA INDEX NAME)



=> d all hitstr 154 tot

L54 ANSWER 1 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN
 AN 2004:1153318 HCAPLUS
 DN 142:176307
 ED Entered STN: 30 Dec 2004
 TI Reaction of Thiols with N-Bonded Sulfenamide Complexes of
 Cobalt(III): Steric Effect and Reaction Pathway
 AU Sisley, Margaret J.; Ferguson, Michael J.; Jordan, Robert B.
 CS Department of Chemistry and X-ray Crystallography Laboratory, University
 of Alberta, Edmonton, AB, T6G 2G2, Can.
 SO Inorganic Chemistry (2005), 44(2), 293-299
 CODEN: INOCAJ; ISSN: 0020-1669
 PB American Chemical Society
 DT Journal
 LA English
 CC 22-4 (Physical Organic Chemistry)
 Section cross-reference(s): 67, 75
 AB The products and kinetics of the reaction of several thiols (RSH
 = 2-aminoethanethiol, cysteine, penicillamine, cysteine Et
 ester) with N-bonded sulfenamide complexes ([Co(en)2(NH2S(CH2)2NH2)]3+
 (IA), [Co(en)2(NH2SCH2CH(CO2H)NH2)]3+ (IC), [Co(en)2(NH2SC(CH3)2CH(CO2H)NH
 2)]3+ (IP)) have been studied. The reaction proceeds by nucleophilic
 attack at sulfur with cleavage of the N-S bond to form a disulfide and
 leave a coordinated NH3 ligand. The kinetics (pH 4-10) reveal that the
 deprotonated thiol, RS-, is the reactive nucleophile and that
 the N-deprotonated sulfenamide complex is unreactive. The reactions of IP
 are approx.104 times slower than those of IA or IC, and the reasons and
 consequences of this large steric effect are discussed. It is concluded,
 on the basis of these and other observations from the literature, that
 there will be substantial steric retardation to nucleophilic attack at
 two-coordinate sulfur in a R-C(CH3)2-S-X-R' unit because of the
 regioselectivity of the reaction. The acid dissociation consts. of IP and the
 X-ray structure of its bromide salt also are reported.
 ST thiol reaction sulfenamide cobalt complex kinetics mechanism
 steric effect
 IT Substitution reaction, nucleophilic
 (at two-coordinate sulfur; steric effect on nucleophilic substitution
 reaction of thiols with N-bonded sulfenamide
 complexes of cobalt(III))
 IT Ionization constant
 (of Co sulfenamide complexes; steric effect on nucleophilic
 substitution reaction of thiols with N-bonded sulfenamide
 complexes of cobalt(III))
 IT Crystal structure
 Molecular structure
 (of cobalt-sulfenamide complex derived from racemic penicillamine;
 steric effect on nucleophilic substitution reaction of thiols
 with N-bonded sulfenamide complexes of cobalt(III))
 IT Reaction kinetics
 Steric effects
 (steric effect on nucleophilic substitution reaction of thiols
 with N-bonded sulfenamide complexes of cobalt(III))
 IT Thiols, reactions
 RL: CPS (Chemical process); PEP (Physical, engineering or chemical
 process); PRP (Properties); RCT (Reactant); PROC (Process);

RACT (Reactant or reagent)
 (steric effect on nucleophilic substitution reaction of **thiols** with N-bonded sulfenamide complexes of cobalt(III))

IT Disulfides
 RL: FMU (Formation, unclassified); FORM (Formation, nonpreparative)
 (steric effect on nucleophilic substitution reaction of **thiols** with N-bonded sulfenamide complexes of cobalt(III))

IT Amides, reactions
Sulfenyl compounds
 RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process);
RACT (Reactant or reagent)
 (sulfenamides, Co complexes; steric effect on nucleophilic substitution reaction of **thiols** with N-bonded sulfenamide complexes of cobalt(III))

IT Exchange reaction
 (thiol/disulfide; steric effect on nucleophilic substitution reaction of **thiols** with N-bonded **sulfenamide** complexes of cobalt(III))

IT 835596-65-1
 RL: PRP (Properties)
 (crystallog.; steric effect on nucleophilic substitution reaction of **thiols** with N-bonded sulfenamide complexes of cobalt(III))

IT 835596-67-3
 RL: CPS (Chemical process); FMU (Formation, unclassified); PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); FORM (Formation, nonpreparative); PROC (Process); **RACT (Reactant or reagent)**
 (reduction kinetics; steric effect on nucleophilic substitution reaction of **thiols** with N-bonded sulfenamide complexes of cobalt(III))

IT 52-66-4 52-67-5, D-Penicillamine 52-90-4, L-Cysteine, reactions 60-23-1, 2-Aminoethanethiol 3411-58-3, L-Cysteine ethyl ester 754200-88-9 754200-93-6 754200-94-7
 RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process);
RACT (Reactant or reagent)
 (steric effect on nucleophilic substitution reaction of **thiols** with N-bonded sulfenamide complexes of cobalt(III))

IT 51-85-4, Cystamine 835596-66-2
 RL: FMU (Formation, unclassified); FORM (Formation, nonpreparative)
 (steric effect on nucleophilic substitution reaction of **thiols** with N-bonded sulfenamide complexes of cobalt(III))

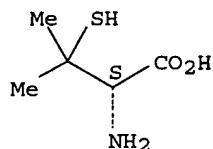
RE.CNT 33 THERE ARE 33 CITED REFERENCES AVAILABLE FOR THIS RECORD
 RE

- (1) Aida, M; Chem Phys Lett 1984, V112, P129 HCAPLUS
- (2) Bachrach, S; J Org Chem 2001, V66, P2005 HCAPLUS
- (3) Bachrach, S; J Org Chem 2002, V67, P8983 HCAPLUS
- (4) Bachrach, S; J Org Chem 2003, V68, P4747
- (5) Bachrach, S; J Phys Chem 1996, V100, P3535 HCAPLUS
- (6) Benesch, R; J Am Chem Soc 1955, V77, P5877 HCAPLUS
- (7) Buckingham, D; Aust J Chem 1967, V20, P257 HCAPLUS
- (8) Dalman, G; J Org Chem 1964, V29, P1480 HCAPLUS
- (9) Decollo, T; J Org Chem 2001, V66, P4244 HCAPLUS
- (10) Fernandes, P; Chem-Eur J 2004, V10, P257 HCAPLUS
- (11) Freter, R; J Org Chem 1979, V44, P1771 HCAPLUS
- (12) Gainsford, G; Chem Commun 1981, P875 HCAPLUS
- (13) Gainsford, G; J Am Chem Soc 1977, V99, P2383 HCAPLUS
- (14) Gainsford, G; J Am Chem Soc 1979, V101, P3966 HCAPLUS
- (15) Hayes, J; J Phys Chem 2003, V107, P7952 HCAPLUS
- (16) Jackson, W; Chem Commun 1977, P199 HCAPLUS
- (17) Kice, J; J Org Chem 1992, V57, P3298 HCAPLUS
- (18) Martin, R; Arch Biochem Biophys 1971, V142, P445
- (19) Pappas, J; J Am Chem Soc 1977, V99, P2926 HCAPLUS
- (20) Patel, H; J Chem Soc, Perkin Trans 2 1990, V37
- (21) Pryor, W; J Am Chem Soc 1970, V92, P2731 HCAPLUS
- (22) Przystas, T; J Am Chem Soc 1973, V95, P5545 HCAPLUS

- (23) Reuben, D; J Am Chem Soc 1976, V98, P114 HCAPLUS
 (24) Reynolds, M; Inorg Chem 1983, V22, P3632 HCAPLUS
 (25) Rosenfield, R; J Am Chem Soc 1977, V99, P4860 HCAPLUS
 (26) Sheldrick, G; Acta Crystallogr 1990, VA46, P467 HCAPLUS
 (27) Sheldrick, G; SHELXL-93; Program for crystal structure determination 1993
 (28) Singh, R; J Am Chem Soc 1990, V112, P1190 HCAPLUS
 (29) Sisley, M; Inorg Chem 2004, V43, P5339 HCAPLUS
 (30) Szajewski, R; J Am Chem Soc 1980, V102, P2011 HCAPLUS
 (31) Theriault, Y; Can J Chem 1985, V63, P2225 HCAPLUS
 (32) Toppen, D; Inorg Chem 1971, V10, P2635 HCAPLUS
 (33) Toteva, M; J Am Chem Soc 2000, V122, P11073 HCAPLUS

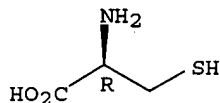
IT 52-67-5, D-Penicillamine 52-90-4, L-Cysteine, reactions
 60-23-1, 2-Aminoethanethiol
 RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process);
 RACT (Reactant or reagent)
 (steric effect on nucleophilic substitution reaction of thiols with N-bonded sulfenamide complexes of cobalt(III))
 RN 52-67-5 HCAPLUS
 CN D-Valine, 3-mercapto- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 52-90-4 HCAPLUS
 CN L-Cysteine (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 60-23-1 HCAPLUS
 CN Ethanethiol, 2-amino- (8CI, 9CI) (CA INDEX NAME)

$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{SH}$

L54 ANSWER 2 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN
 AN 2003:891789 HCAPLUS
 DN 140:77215
 ED Entered STN: 14 Nov 2003
 TI Reaction of stable sulfenic and selenenic acids containing a bowl-type steric protection group with a phosphine. Elucidation of the mechanism of reduction of sulfenic and selenenic acids
 AU Goto, Kei; Shimada, Keiichi; Nagahama, Michiko; Okazaki, Renji; Kawashima, Takayuki
 CS Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo, 113-0033, Japan
 SO Chemistry Letters (2003), 32(11), 1080-1081
 CODEN: CMLTAG; ISSN: 0366-7022
 PB Chemical Society of Japan
 DT Journal
 LA English

- CC 29-8 (Organometallic and Organometalloidal Compounds)
Section cross-reference(s): 22
- AB The mechanism of the reduction of the stable sulfenic acid and selenenic acid containing a bowl-type steric protection group, 2,6-[2,6-(2,6-Me₂C₆H₃)₂C₆H₃CH₂]₂-4-tBuC₆H₂EOH (2,6-R₂-4-tBuC₆H₂EOH, 1, 2, E = S, Se) by triphenylphosphine was examined by tracer studies using H₂18O. Oxidation of PPh₃ by 1 and 2 in H₂18O (19.2% content 18O) produced 2,6-R₂-4-tBuC₆H₂EH (4, 6, E = S and Se, resp.) and 18OPPh₃; the isotope content in the oxide corresponds to 77% and 87% exchange rates, resp. These high exchange rates indicate, that the initial step of the reaction involves the attack of the phosphine on the sulfur or selenium atom of 1 and 2, resp., to give the 2,6-R₂-4-tBuC₆H₂EP+Ph₃ phosphonium intermediate which adds reversibly OH⁻ from the reaction media and eliminates 4 or 6. This behavior contrasts with the reduction of tBuOOH by a phosphine, where the initial attack occurs on the hydroxylic oxygen.
- ST sulfenic selenenic acid phosphine oxidn mechanism; thiol phosphine oxide formation mechanism sulfenic acid oxidn; selenol phosphine oxide formation mechanism selenenic acid oxidn
- IT **Exchange reaction**
(isotope, oxygen-18; mechanism of triphenylphosphine oxidation by sterically protected sulfenic and selenenic acids, oxygen isotope exchange with water)
- IT **Selenenic acids**
Sulfenic acids
RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
(mechanism of triphenylphosphine oxidation by sterically protected sulfenic and selenenic acids)
- IT **Reduction**
(mechanism; of sterically protected sulfenic and selenenic acids by triphenylphosphine, oxygen-18 isotope exchange)
- IT **Oxidation**
(of triphenylphosphine by sterically protected sulfenic and selenenic acids, oxygen-18 isotope exchange)
- IT 98511-61-6
RL: CPS (Chemical process); FMU (Formation, unclassified); PEP (Physical, engineering or chemical process); FORM (Formation, nonpreparative); PROC (Process)
(oxidation, oxygen isotope exchange; mechanism of triphenylphosphine oxidation by sterically protected sulfenic and selenenic acids, oxygen isotope exchange with water)
- IT 603-35-0, Triphenylphosphine, reactions
RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
(oxidation, oxygen isotope exchange; mechanism of triphenylphosphine oxidation by sterically protected sulfenic and selenenic acids, oxygen isotope exchange with water)
- IT 177971-45-8 380305-90-8
RL: FMU (Formation, unclassified); FORM (Formation, nonpreparative)
(reduction product; mechanism of triphenylphosphine oxidation by sterically protected sulfenic and selenenic acids, oxygen isotope exchange with water)
- IT 186256-53-1 380305-91-9
RL: RCT (Reactant); RACT (Reactant or reagent)
(reduction; mechanism of triphenylphosphine oxidation by sterically protected sulfenic and selenenic acids, oxygen isotope exchange with water)
- RE.CNT 22 THERE ARE 22 CITED REFERENCES AVAILABLE FOR THIS RECORD
- RE
- (1) Allison, W; Acc Chem Res 1976, V9, P293 HCAPLUS
 - (2) Anon; Organoselenium Chemistry 1987
 - (3) Anon; The Chemistry of Organic Selenium and Tellurium Compounds 1986, V1
 - (4) Anon; The Chemistry of Organic Selenium and Tellurium Compounds 1987, V2
 - (5) Claiborne, A; Adv Protein Chem 2001, V58, P215 HCAPLUS
 - (6) Cooper, R; J Am Chem Soc 1970, V92, P2575 HCAPLUS
 - (7) Denney, D; J Am Chem Soc 1960, V82, P1393 HCAPLUS
 - (8) Flohe, L; Signal Transduction by Reactive Oxygen and Nitrogen Species:

Pathways and Chemical Principles 2003

- (9) Ganter, H; Methods in Enzymology 1984, V107, P593
- (10) Goto, K; Chem Lett V2001, P1204
- (11) Goto, K; J Am Chem Soc 1997, V119, P1460 HCAPLUS
- (12) Goto, K; Liebigs Ann/Recl V1997, P2393
- (13) Goto, K; Org Lett 2001, V3, P3569 HCAPLUS
- (14) Goto, K; Tetrahedron Lett 2000, V41, P8479 HCAPLUS
- (15) Hatfield, L; Tetrahedron Lett V1970, P4897
- (16) Hiatt, R; Can J Chem 1971, V49, P1707 HCAPLUS
- (17) Hogg, D; The Chemistry of Sulfenic Acids and Their Derivatives 1990, P361 HCAPLUS
- (18) Ishii, A; J Org Chem 1999, V64, P1084 HCAPLUS
- (19) Kice, J; Adv Phys Org Chem 1980, V17, P65 HCAPLUS
- (20) Kirby, A; The Organic Chemistry of Phosphorus 1967, P72
- (21) Saiki, T; Angew Chem, Int Ed Engl 1997, V36, P2223 HCAPLUS
- (22) Shulman, J; J Org Chem 1977, V42, P3970 HCAPLUS

L54 ANSWER 3 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN

AN 2002:269384 HCAPLUS

DN 136:401369

ED Entered STN: 11 Apr 2002

TI Mechanism of the Second Sulfenylation of Indole

AU Hamel, Pierre

CS The Merck Frosst Centre for Therapeutic Research, Pointe-Claire-Dorval, QC, H9R 4P8, Can.

SO Journal of Organic Chemistry (2002), 67(9), 2854-2858

CODEN: JOCEAH; ISSN: 0022-3263

PB American Chemical Society

DT Journal

LA English

CC 22-6 (Physical Organic Chemistry)

OS CASREACT 136:401369

AB Sulfenylation of indole using a sulfenyl chloride occurs initially at the 3-position of the ring, leading to a 3-indolyl sulfide. When an excess of sulfenyl chloride is used, a second sulfide group is introduced at the 2-position, and an indolyl 2,3-bis-sulfide results. We have demonstrated that this second sulfenylation occurs not by direct introduction of the second sulfide at the 2-position but via initial formation of an indolenium 3,3-bis-sulfide intermediate, followed by migration of one of the sulfide groups to the 2-position. This was achieved by the isolation of two examples of 3H-indole 3,3-bis-sulfides and by subsequent demonstration that they rearrange to the indolyl 2,3-bis-sulfides by treatment with sulfenyl halides.

ST indole sulfenylation mechanism

IT Rearrangement

(of 3H-indole 3,3-bis-sulfides; mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT Sulfenyl compounds

RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)

(sulfenyl chlorides; mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT Substitution reaction

(sulfenylation; mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT Quaternization

(using sulfenyl chloride; mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT 120-72-9, Indole, reactions 54491-43-9, 3-(Phenylthio)indole

RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); RCT (Reactant); PROC (Process); RACT (Reactant or reagent) (mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT 931-59-9P, Benzenesulfenyl chloride 933-00-6P, p-Toluenesulfenyl chloride

RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)
(mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT 120517-31-9, 2-(Phenylthio)indole

RL: RCT (Reactant); RACT (Reactant or reagent)
(mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT 647024-85-9P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT 70291-88-2P, 2,3-Bis(phenylthio)indole 200617-54-5P,
3-(Phenylthio)-3-(p-tolylthio)-3H-indole 431878-78-3P,
3-(Phenylthio)-2-(p-tolylthio)indole 431878-79-4P, 2-(Phenylthio)-3-(p-tolylthio)indole 431878-81-8P, 2,3,3-Tris(phenylthio)-3H-indole
RL: SPN (Synthetic preparation); PREP (Preparation)
(mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT 200617-53-4P, 3,3-Bis(phenylthio)-3H-indole

RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)
(rearrangement; mechanism of the second sulfenylation of indole with sulfenyl chlorides)

IT 431878-80-7P, 2,3-Bis(p-tolylthio)indole

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(regioselective desulfenylation; mechanism of the second sulfenylation of indole with sulfenyl chlorides)

RE.CNT 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE

- (1) Anzai, K; J Heterocycl Chem 1979, V16, P567 HCAPLUS
- (2) Atkinson, J; Synthesis 1988, P480 HCAPLUS
- (3) Friesen, R; Tetrahedron Lett 1985, V26, P161 HCAPLUS
- (4) Gassman, P; J Am Chem Soc 1974, V96, P549
- (5) Hamel, P; J Org Chem 1992, V57, P2994
- (6) Hamel, P; J Org Chem 1994, V59, P6372 HCAPLUS
- (7) Hamel, P; J Org Chem 1996, V61, P1573 HCAPLUS
- (8) Hamel, P; Tetrahedron Lett 1997, V38, P8473 HCAPLUS
- (9) Jones, R; Comprehensive Heterocyclic Chemistry 1984, V4, P201
- (10) Plate, R; Tetrahedron 1986, V42, P4503 HCAPLUS
- (11) Plate, R; Tetrahedron 1986, V42, P4511 HCAPLUS
- (12) Raban, M; J Org Chem 1980, V45, P1688 HCAPLUS
- (13) Vice, S; Tetrahedron Lett 1985, V26, P165 HCAPLUS
- (14) Wieland, T; Chem Ber 1963, V96, P260 HCAPLUS

IT 931-59-9P, Benzenesulfenyl chloride

RL: CPS (Chemical process); PEP (Physical, engineering or chemical process); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); PROC (Process); RACT (Reactant or reagent)
(mechanism of the second sulfenylation of indole with sulfenyl chlorides)

RN 931-59-9 HCAPLUS

CN Benzenesulfenyl chloride (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)

Ph-S-Cl

L54 ANSWER 4 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN

AN 2000:85193 HCAPLUS

DN 132:207478

ED Entered STN: 04 Feb 2000

Search done by Ross Schipe

TI A new sulfenylation reagent, 3-phenylsulfenyl-2-(N-cyanoimino)thiazolidine, and its optically active version
 AU Tanaka, Tetsuaki; Azuma, Tsutomu; Fang, Xie; Uchida, Shuji; Iwata, Chuzo; Ishida, Toshimasa; In, Yasuko; Maezaki, Naoyoshi
 CS Graduate School Pharmaceutical Sciences, Osaka Univ., Suita, 565, Japan
 SO Synlett (2000), (1), 33-36
 CODEN: SYNLES; ISSN: 0936-5214
 PB Georg Thieme Verlag
 DT Journal
 LA English
 CC 21-2 (General Organic Chemistry)
 Section cross-reference(s): 75
 OS CASREACT 132:207478
 AB A new sulfenylation reagent, 3-(phenylthio)-2-(N-cyanoimino)thiazolidine (I), was developed, which is readily available and stable upon storage. Compound I easily reacts with amines or thiols to give the corresponding sulfenamides or asym. disulfides in excellent yields. The α -sulfenylation of carbonyl compds. with I proceeds smoothly. Furthermore, the optically active 4-diphenylmethyl derivative of I was synthesized as an asym. sulfenylation reagent, which realized 96% ee upon α -sulfenylation of a cyclic β -keto ester.
 ST phenyl cyaniminiothiazolidinyl sulfide sulfenylation reagent prepn; phenylsulfenylcyaniminiothiazolidine stereoselective sulfenylation reagent; amine phenylsulfenylcyaniminiothiazolidine sulfenylation; thiol phenylsulfenylcyaniminiothiazolidine sulfenylation; sulfenamide prepn; disulfide prepn; ketone phenylsulfenylcyaniminiothiazolidine sulfenylation
 IT Thioethers
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (oxo; sulfenylation with (phenylthio)(cyanimino)thiazolidine as reagent)
 IT Amides, preparation
 Amides, preparation
 Sulfenyl compounds
 Sulfenyl compounds
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (sulfenamides; sulfenylation with (phenylthio)(cyanimino)thiazolidine as reagent)
 IT Amines, reactions
 Reagents
 Thiols (organic), reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation with (phenylthio)(cyanimino)thiazolidine as reagent)
 IT Ketones, preparation
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (sulfenylation with (phenylthio)(cyanimino)thiazolidine as reagent)
 IT Disulfides
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (sulfenylation with (phenylthio)(cyanimino)thiazolidine as reagent)
 IT Addition reaction
 Substitution reaction
 (sulfenylation; sulfenylation with (phenylthio)(cyanimino)thiazolidine as reagent)
 IT 258823-04-0P
 RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
 (crystal structure)
 IT 35874-99-8P 76643-99-7P 84978-78-9P
 RL: BYP (Byproduct); PREP (Preparation)
 (disulfenylation byproducts from the preparation of monosulfenylated ketones with (phenylthio)(cyanimino)thiazolidine as reagent)
 IT 868-59-7 10191-60-3
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (preparation of (phenylthio)(cyanimino)thiazolidine as stereoselective sulfenylation reagent)
 IT 258822-90-1P 258822-91-2P 258822-92-3P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)
 (preparation of (phenylthio)(cyanimino)thiazolidine as stereoselective sulfenylation reagent)

IT 258822-93-4P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (stereoselective sulfenylation reagent)

IT 258823-03-9P
 RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
 (stereoselective sulfenylation with (phenylthio)(cyanimino)thiazolidine)

IT 609-14-3, Ethyl α -methylacetoacetate 874-23-7,
 2-Acetylcyclohexanone 1655-07-8, Ethyl 2-oxocyclohexanecarboxylate
 3580-38-9, 2-Benzoylcyclohexanone 4513-77-3, 2-Cyanocyclohexanone
 10472-24-9 41043-87-2, 2-Pivaloylcyclohexanone 41302-34-5, Methyl
 2-oxocyclohexanecarboxylate 52784-32-4 98969-09-6 258822-94-5
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (stereoselective sulfenylation with (phenylthio)(cyanimino)thiazolidine)

IT 65755-68-2P 72302-36-4P 98711-81-0P 258822-95-6P 258822-96-7P
 258822-97-8P 258822-98-9P 258822-99-0P 258823-00-6P 258823-01-7P
 258823-02-8P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (stereoselective sulfenylation with (phenylthio)(cyanimino)thiazolidine)

IT 258822-89-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation reagent)

IT 62-53-3, Phenylamine, reactions 75-04-7, Ethylamine, reactions
 75-08-1, Ethanethiol 75-64-9, tert-Butylamine,
 reactions 100-46-9, Benzylamine, reactions 108-91-8, Cyclohexylamine,
 reactions 108-94-1, Cyclohexanone, reactions 110-89-4, Piperidine,
 reactions 120-92-3, Cyclopentanone 123-75-1, Pyrrolidine, reactions
 141-97-9, Ethyl acetoacetate 502-42-1, Cycloheptanone 529-34-0,
 1-Tetralone 583-60-8, 2-Methylcyclohexanone 26445-03-4
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation with (phenylthio)(cyanimino)thiazolidine as reagent)

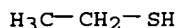
IT 4032-81-9P 14933-91-6P 19117-31-8P 20841-46-7P 23837-23-2P
 24380-80-1P 27872-73-7P 27920-40-7P, 2-(Phenylthio)cyclohexanone
 29959-86-2P 34780-06-8P 36476-32-1P 52190-40-6P,
 2-(Phenylthio)cyclopentanone 52190-41-7P, 2-(Phenylthio)cycloheptanone
 54376-46-4P, 2-Methyl-2-(phenylthio)cyclohexanone 79581-44-5P
 95156-44-8P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (sulfenylation with (phenylthio)(cyanimino)thiazolidine as reagent)

RE.CNT 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD

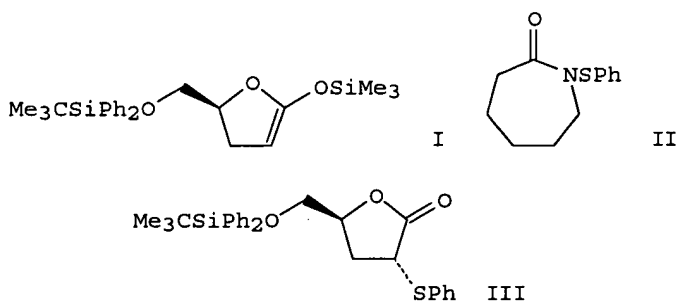
RE

- (1) Alexander, R; Tetrahedron Lett 1985, V26, P5339 HCAPLUS
- (2) Boustany, K; Tetrahedron Lett 1970, P3547 HCAPLUS
- (3) Caputo, R; Synthesis 1989, P464 HCAPLUS
- (4) Chibale, K; Tetrahedron Lett 1994, V35, P3991 HCAPLUS
- (5) Foray, G; Tetrahedron Lett 1997, V38, P2035 HCAPLUS
- (6) Fujisawa, T; Chem Lett 1973, P287 HCAPLUS
- (7) Harpp, D; Tetrahedron Lett 1970, P3551 HCAPLUS
- (8) Harpp, D; Tetrahedron Lett 1971, P4953 HCAPLUS
- (9) Hiroi, K; Chem Lett 1979, P969 HCAPLUS
- (10) Iwata, C; Heterocycles 1988, V27, P323 HCAPLUS
- (11) Iwata, C; Heterocycles 1990, V31, P1601 HCAPLUS
- (12) Iwata, C; Heterocycles 1991, V32, P2471 HCAPLUS
- (13) Iwata, C; J Chem Soc, Chem Commun 1992, P1379 HCAPLUS
- (14) Iwata, C; Synthesis 1988, P261 HCAPLUS
- (15) Kumamoto, T; Bull Chem Soc Jpn 1972, V45, P866 HCAPLUS
- (16) Mukaiyama, T; Tetrahedron Lett 1970, P5115 HCAPLUS
- (17) Murai, S; J Chem Soc, Chem Commun 1972, P946 HCAPLUS
- (18) Neidlein, R; Arch Pharm 1972, V305, P731 HCAPLUS
- (19) Orena, M; Tetrahedron Lett 1992, V33, P3797 HCAPLUS

(20) Paterson, I; Synlett 1991, P145 HCAPLUS
 (21) Seebach, D; Tetrahedron Lett 1973, P5113 HCAPLUS
 (22) Tanaka, T; Heterocycles 1996, V42, P265 HCAPLUS
 (23) Tanaka, T; J Chem Soc, Chem Commun 1994, P2301 HCAPLUS
 (24) Tanaka, T; Synlett 1997, P316 HCAPLUS
 (25) Trost, B; Chem Rev 1978, V78, P363 HCAPLUS
 (26) Trost, B; J Am Chem Soc 1976, V98, P4887 HCAPLUS
 (27) Yura, T; Chem Lett 1986, P1809 HCAPLUS
 IT 75-08-1, Ethanethiol
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation with (phenylthio)(cyanimino)thiazolidine as reagent)
 RN 75-08-1 HCAPLUS
 CN Ethanethiol (8CI, 9CI) (CA INDEX NAME)



L54 ANSWER 5 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN
 AN 1992:151460 HCAPLUS
 DN 116:151460
 ED Entered STN: 17 Apr 1992
 TI Diastereoselective sulfenylation reactions employing N-phenylthio lactams under nonbasic conditions
 AU Wilson, Lawrence J.; Liotta, Dennis C.
 CS Dep. Chem., Emory Univ., Atlanta, GA, 30322, USA
 SO Journal of Organic Chemistry (1992), 57(7), 1948-50
 CODEN: JOCEAH; ISSN: 0022-3263
 DT Journal
 LA English
 CC 27-6 (Heterocyclic Compounds (One Hetero Atom))
 OS CASREACT 116:151460
 GI



AB Silyl enol ethers and silyl ketene acetals react with sulfenamides in the presence of trimethylsilyl triflate to give the corresponding trans-sulfenylated ketones and lactones. The stereoselectivity observed in these reactions is good to excellent and appears to be governed by steric factors. Thus, the silyl ketene acetal I reacted with N-phenylthio-ε-caprolactam II in presence of trimethylsilyl triflate to give 82% trans-sulfenylated lactone III and 10% of cis-sulfenylated lactone.
 ST lactone sulfenylation phenylthiolactam stereoselectivity; ketone sulfenylation phenylthiolactam stereoselectivity
 IT Stereochemistry
 (of sulfenylation of ketones and lactones via silyl enol ethers and silyl ketene acetals and phenylthiolactams)

IT Substitution reaction
(sulfenylation, stereoselective, of ketones and lactones via silyl enol ethers and silyl ketene acetals with phenylthiolactams)

IT 125440-13-3
RL: RCT (Reactant); RACT (Reactant or reagent)
(diastereoselective sulfenylation of, with phenylthiolactams)

IT 36452-23-0P 139524-50-8P 139524-51-9P 139524-52-0P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and diastereoselective sulfenylation by, of silyl enol ethers and silyl ketene acetals)

IT 931-59-9P, Benzenesulfonyl chloride
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and sulfenylation by, of dimethylpiperidinone)

IT 52190-40-6P 62675-41-6P 62675-50-7P 63608-45-7P 66032-98-2P
66032-99-3P 73843-08-0P 129778-50-3P 129778-55-8P 139524-53-1P
139524-54-2P 139524-55-3P 139563-96-5P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

IT 98-53-3 583-60-8 130745-59-4
RL: RCT (Reactant); RACT (Reactant or reagent)
(sequential conversion to silyl enol ether and sulfenylation of, with phenylthiolactam)

IT 108-29-2
RL: RCT (Reactant); RACT (Reactant or reagent)
(sequential conversion to silyl ketene acetal and diastereoselective sulfenylation of, with phenylthiolactam)

IT 102717-29-3
RL: RCT (Reactant); RACT (Reactant or reagent)
(sequential conversion to silyl ketene acetal and diastereoselective sulfenylation of, with phenylthiolactams)

IT 19980-43-9
RL: RCT (Reactant); RACT (Reactant or reagent)
(sulfenylation of)

IT 139524-56-4
RL: RCT (Reactant); RACT (Reactant or reagent)
(N-sulfenylation of, with phenylsulfonyl chloride)

IT 931-59-9P, Benzenesulfonyl chloride
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and sulfenylation by, of dimethylpiperidinone)

RN 931-59-9 HCAPLUS

CN Benzenesulfonyl chloride (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)

Ph-S-Cl

L54 ANSWER 6 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN

AN 1991:121017 HCAPLUS

DN 114:121017

ED Entered STN: 06 Apr 1991

TI Mechanistic aspects of nucleophilic substitutions of sulfenic acid derivatives

AU Okuyama, Tadashi

CS Fac. Eng. Sci., Osaka Univ., Toyonaka, 560, Japan

SO Chem. Sulphenic Acids Their Deriv. (1990), 743-63. Editor(s): Patai, Saul. Publisher: Wiley, Chichester, UK.
CODEN: 57ARAT

DT Conference; General Review

LA English

CC 22-0 (Physical Organic Chemistry)

AB Sulfenium ion intermediates; bimol. nucleophilic substitution of sulfonyl halides, sulfenyl esters, and disulfides; 70 refs.

ST review sulfenic acid nucleophile substitution

IT Sulfenic acids

RL: RCT (Reactant); RACT (Reactant or reagent)
 (derivs., nucleophilic substitution of, mechanism of)

IT Disulfides
 Sulfenyl halides
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (nucleophilic substitution of, mechanism of)

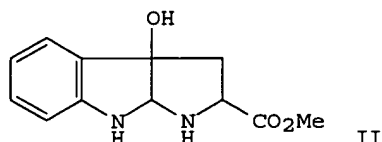
IT Substitution reaction, nucleophilic
 (of sulfenic acid derivs., mechanism of)

IT Thiols, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfonate and sulfinic acid derivs., nucleophilic substitution of,
 mechanism of)

IT Sulfenic acids
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (esters, nucleophilic substitution of, mechanism of)

IT 18155-21-0D, Sulfonium, derivs.
 RL: PROC (Process)

L54 ANSWER 7 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN
 AN 1987:497110 HCAPLUS
 DN 107:97110
 ED Entered STN: 19 Sep 1987
 TI Analgesic dipeptide derivatives. 3. Synthesis and structure-activity
 relationships of o-nitrophenyl-modified analogs of the analgesic compound
 H-Lys-Trp(NPS)-OMe
 AU Garcia-Lopez, M. Teresa; Gonzalez-Muniz, Rosario; Molinero, M. Teresa;
 Naranjo, Jose R.; Del Rio, J.
 CS Inst. Quim. Med., CSIC, Madrid, 28006, Spain
 SO Journal of Medicinal Chemistry (1987), 30(9), 1658-63
 CODEN: JMCMAR; ISSN: 0022-2623
 DT Journal
 LA English
 CC 34-3 (Amino Acids, Peptides, and Proteins)
 Section cross-reference(s): 1
 OS CASREACT 107:97110
 GI



AB Title dipeptides H-Lys-Trp(SR)-OMe [I; R = Ph, C₆H₄CO₂Me-o, C₆H₄NO₂-p, C₆H₃(NO₂)-2,4] were prepared by sulfonylating Z-Lys(Z)-Trp-OMe (Z = PhCH₂O₂C) with RSOCl and Z-deblocking the resulting Z-Lys(Z)-Trp(SR)-OMe by (CF₃CO₂)₃B/CF₃CO₂H or Me₃SiI/MeCN. I (R = C₆H₄NHAc-o) was prepared from Z-Lys(Z)-Trp(SC₆H₄NO₂-o)-OMe by sequential reduction, N-acetylation, and Z-deblocking. Pyrrolol[2,3-b]indole II was treated with Me₃CSH and HSCH₂CH₂CO₂Me to give H-Trp(SCMe₃)-OMe and H-Trp(SCH₂CH₂CO₂Me)-OMe, resp., which were used in the synthesis of I (R = CMe₃ and CH₂CH₂CO₂Me, resp.). I (R = C₆H₄CO₂Me-o) elicited a naloxone-reversible antinociceptive effect in mice similar to that of the analgesic dipeptide I (R = C₆H₄NO₂-o). No analgesia was observed for the other I. Structure-activity studies indicated that the role of the SC₆H₄NO₂-o and SC₆H₄CO₂Me-o moieties could be related to the adoption of a preferential active conformation.

ST phenylsulfonyl tryptophan dipeptide prepn analgesia; sulfonylation tryptophan dipeptide; structure analgesic phenylsulfonyl tryptophan dipeptide

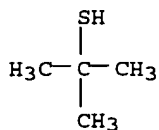
IT Analgesics

(lysyl-(nitrophenylsulfenyl)tryptophan Me ester analogs)
 IT Molecular structure-biological activity relationship
 (analgesic, of lysyl-(nitrophenylsulfenyl)tryptophan Me ester analogs)
 IT Substitution reaction
 (sulfenylation, of tryptophan-containing dipeptide)
 IT 109064-70-2
 RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); BIOL (Biological study)
 (analgesic activity of)
 IT 5459-63-2
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (disulfide cleavage-S-chlorination of)
 IT 6066-82-6, N-Hydroxysuccinimide
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (esterification by, of lysine derivative)
 IT 405-39-0
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (esterification of, with hydroxysuccinimide)
 IT 109064-77-9P 109064-78-0P 109064-79-1P 109064-80-4P 109064-81-5P
 109064-85-9P
 RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); BIOL (Biological study); PREP (Preparation)
 (preparation and analgesic activity of)
 IT 109064-72-4P 109064-73-5P 109064-74-6P 109064-75-7P 109064-76-8P
 109064-84-8P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (preparation and deblocking of)
 IT 109064-86-0P 109064-87-1P 109064-88-2P 109064-89-3P 109064-90-6P
 109064-91-7P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (preparation and peptide coupling of, with lysine derivative)
 IT 21160-83-8P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (preparation and peptide coupling of, with tryptophan derivs.)
 IT 109064-82-6P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (preparation and reduction of)
 IT 78880-71-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation and sulfenylation by, of tryptophan-containing dipeptide)
 IT 109064-83-7P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
 (preparation and N-acetylation of)
 IT 7652-46-2
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with tryptophan-containing dipeptide)
 IT 75-66-1, tert-Butylthiol 2935-90-2,
 3-Mercaptopropionic acid methyl ester
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (ring cleavage by, of hexahydropyrroloindole derivative)
 IT 51440-62-1
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (ring cleavage of, by thiols)
 IT 528-76-7 931-59-9 937-32-6 7669-54-7
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation by, of tryptophan-containing dipeptide)
 IT 52126-94-0
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation of)
 IT 75-66-1, tert-Butylthiol

RL: RCT (Reactant); RACT (Reactant or reagent)
(ring cleavage by, of hexahydropyrroloindole derivative)

RN 75-66-1 HCAPLUS

CN 2-Propanethiol, 2-methyl- (8CI, 9CI) (CA INDEX NAME)

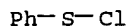


IT 931-59-9

RL: RCT (Reactant); RACT (Reactant or reagent)
(sulfenylation by, of tryptophan-containing dipeptide)

RN 931-59-9 HCAPLUS

CN Benzenesulfonyl chloride (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)



L54 ANSWER 8 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN

AN 1981:514988 HCAPLUS

DN 95:114988

ED Entered STN: 12 May 1984

TI Participation of electrophilic organic compounds of sulfur(II) in catalytic conversions. II. Catalytic exchange reaction of N-monosulfenated amines with S-esters of thiocarboxylic acids

AU Parfenov, E. A.; Fomin, V. A.

CS Vses. Nauchno-Issled. Vitam. Inst., Moscow, USSR

SO Zhurnal Obshchei Khimii (1981), 51(5), 1129-37

CODEN: ZOKHA4; ISSN: 0044-460X

DT Journal

LA Russian

CC 25-18 (Noncondensed Aromatic Compounds)

Section cross-reference(s): 6

AB RSX (R = Ph, 2-O₂NC₆H₄; X = Cl, Br) reacted with R₁R₂NH (R₁R₂N = piperidino, morpholino, PhNH, PhNMe, α-C₁₀H₇NH, carbazolyl, benzimidazolyl) in the presence of Et₃N to give 8 corresponding RSNR₁R₂ (I) in 32-88% yield. I reacted with 6 R₃COSR₄ (R₃ = Me, Ph, CH₂:CHCH₂CH₂, 3-pyridyl; R₄ = CH₂Ph, Ph, C₆H₄NO₂-2 and -4) in the presence of a soft base [Ph₃P, P(OMe)₃, P(OPh)₃] to give 9 corresponding R₃CONR₁R₂ and RSSR₄ in ≥81% yield. This is a model reaction for energy transfer in living systems.

ST energy transfer model living system; exchange reaction sulfenamide thiocarboxylate

IT Energy transfer

(in living systems, exchange reaction of sulfenamides with thiolcarboxylates as model for)

IT Exchange reaction

(of sulfenamides with thiolcarboxylates, as model for energy transfer in living systems)

IT Sulfenamides

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)

(preparation and exchange reaction of, with thiolcarboxylates)

IT Amines, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
(sulfenylation of)

IT Exchange reaction catalysts

(trivalent phosphorus compds., for sulfenamides with thiolcarboxylates)

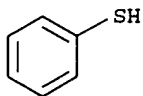
IT Esters, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
 (thiol, exchange reaction of, with sulfenamides)
 IT 98-88-4
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (acylation of nitrothiophenol with)
 IT 112-67-4
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (acylation of toluenethiol with)
 IT 100-53-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (acylation of, with palmitoyl chloride)
 IT 4875-10-9
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (benzoylation of)
 IT 101-02-0 121-45-9 603-35-0, uses and miscellaneous
 RL: CAT (Catalyst use); USES (Uses)
 (catalysts, for exchange reaction of sulfenamides with
 thiolcarboxylates)
 IT 1155-00-6
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (esterification of pyridinecarboxylic acid with)
 IT 59-67-6, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (esterification of, with bis(nitrophenyl) disulfide)
 IT 591-80-0
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (esterification of, with di-Ph disulfide)
 IT 884-09-3P 934-87-2P 15119-62-7P 24197-72-6P 78945-05-8P
 78966-71-9P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
 (Reactant or reagent)
 (preparation and exchange reaction of, with sulfenamides)
 IT 4837-33-6P 7257-62-7P 14933-91-6P 33224-04-3P 66552-58-7P
 78945-06-9P 78945-08-1P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP
 (Preparation); RACT (Reactant or reagent)
 (preparation and exchange reaction of, with thiolcarboxylates)
 IT 93-98-1P 103-84-4P 108-98-5P, preparation 492-85-3P
 618-42-8P 634-42-4P 776-75-0P 1934-92-5P 58170-51-7P 66591-30-8P
 78945-04-7P 78945-07-0P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 IT 882-33-7
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with pentenoic acid)
 IT 98-74-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reduction of, in presence of acetic acid, thioacetate by)
 IT 98-09-9
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reduction of, with red phosphorus in presence of acetic and benzoic acids,
 thiolcarboxylates by)
 IT 22024-99-3 28074-23-9
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation of amines with)
 IT 7669-54-7
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation of carbazole with)
 IT 62-53-3, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation of, with benzene- and nitrobenzenesulfonyl bromide)
 IT 51-17-2 100-61-8, reactions 110-89-4, reactions 110-91-8, reactions
 134-32-7
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation of, with nitrobenzenesulfonyl bromide)
 IT 86-74-8

RL: RCT (Reactant); RACT (Reactant or reagent)
 (sulfenylation of, with nitrobenzenesulfonyl chloride)
 IT 100-53-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (acylation of, with palmitoyl chloride)
 RN 100-53-8 HCAPLUS
 CN Benzenemethanethiol (9CI) (CA INDEX NAME)

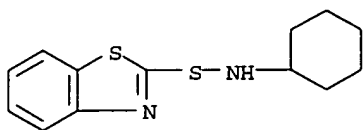
HS-CH₂-Ph

IT 108-98-5P, preparation
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 RN 108-98-5 HCAPLUS
 CN Benzenethiol (8CI, 9CI) (CA INDEX NAME)

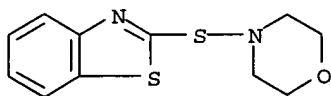


L54 ANSWER 9 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN
 AN 1981:65055 HCAPLUS
 DN 94:65055
 ED Entered STN: 12 May 1984
 TI Reaction of sulfenamides with dialkyl and trialkyl phosphites. An efficient synthesis of phosphoramidates by unusual substitution at the sulfur-nitrogen bond in (2-benzothiazolyl)sulfenamides
 AU Torii, Sigeru; Sayo, Noboru; Tanaka, Hideo
 CS Sch. Eng., Okayama Univ., Okayama, 700, Japan
 SO Chemistry Letters (1980), (6), 695-8
 CODEN: CMLTAG; ISSN: 0366-7022
 DT Journal
 LA English
 CC 23-12 (Aliphatic Compounds)
 Section cross-reference(s): 22
 OS CASREACT 94:65055
 AB Regioselective attack of the trivalent P atom of dialkyl and trialkyl phosphites on either N or S atom of RSNR1R2 (R = Ph, 2-benzothiazolyl; R1, R2 = H, alkyl, NR1R2 = succinimidyl, morpholino) has been found. The reaction of phenylsulfenamides with dialkyl phosphites yielded phosphorothiolates, whereas the treatment of (2-benzothiazolyl)sulfenamides with dialkyl and trialkyl phosphites gave phosphoramidates in excellent yields.
 ST sulfenamide reaction phosphite regioselectivity
 IT Substitution reaction
 (in reaction of sulfenamides with dialkyl and trialkyl phosphites, regioselectivity in)
 IT Stereochemistry
 (regioselectivity, in reaction of sulfenamides with dialkyl and trialkyl phosphites)
 IT 597-24-0P 597-25-1P 1889-58-3P 2672-32-4P 3167-69-9P 4237-00-7P
 4972-36-5P 15267-38-6P 20465-00-3P 22685-19-4P 22685-20-7P
 32405-88-2P 37097-43-1P 53640-96-3P 54480-52-3P 59658-74-1P
 67828-17-5P 68036-32-8P 74124-44-0P 74124-45-1P 74124-46-2P
 74124-48-4P 74124-50-8P 74124-51-9P 74130-08-8P 75291-13-3P
 75291-14-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 IT 95-31-8 95-33-0 102-77-2 2720-65-2 4837-31-4
 10220-34-5 14204-24-1 26773-65-9 26773-69-3 63451-39-8

66552-53-2
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with phosphites)
 IT 691-96-3 762-04-9 868-85-9
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with sulfenamides)
 IT 95-33-0 102-77-2
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with phosphites)
 RN 95-33-0 HCAPLUS
 CN 2-Benzothiazolesulfenamide, N-cyclohexyl- (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)



RN 102-77-2 HCAPLUS
 CN Morpholine, 4-(2-benzothiazolythio)- (9CI) (CA INDEX NAME)



L54 ANSWER 10 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN
 AN 1979:22526 HCAPLUS
 DN 90:22526
 ED Entered STN: 12 May 1984
 TI Action of sulfenyl chlorides on N-alkoxyureas
 AU Demoute, Jean Pierre; Teche, Andre; Perronnet, Jacques
 CS Cent. Rech. Roussel Uclaf, Romainville, Fr.
 SO Journal of Chemical Research, Synopses (1978), (7), 244-5
 CODEN: JRPSDC; ISSN: 0308-2342
 DT Journal
 LA English/French
 CC 25-21 (Noncondensed Aromatic Compounds)
 Section cross-reference(s): 23
 OS CASREACT 90:22526
 AB 3,4-Cl₂C₆H₃NHCONRR₁ (I, R = H, R₁ = MeO) reacted with ClSR₂ (II, R₂ = Et, Me₂CH, Ph, p-O₂NC₆H₄) to give 22-75% I (R = H, R₁ = SR₂). Similar alkylthiolation was observed in the reactions of I (R = H, R₁ = PhCH₂O, EtO) with ClSEt, and of I (R = H, R₁ = PhCH₂O) with ClSCCl₃. I (R = Me₂CHS, PhS, R₁ = Me₃CO; R = Cl₃CS, R₁ = MeO) were obtained in 52-80% yield by the reaction of II (R₂ = Me₂CH, Ph, Cl₃C) with I (R = H; R = Me₃CO, MeO). I (R = Cl₃CS, R₁ = MeO) underwent an elimination reaction on thermolysis to give I (R = Cl₃CS, R₁ = H). The Na salts of I (R = H; R₁ = EtS, PhS) underwent further alkylthiolation with II (R₂ = Et, Ph) to give 23-67% (R = R₁ = EtS, PhS; R = EtS, R₁ = PhS). Similarly, O-methyl-N-acylhydroxylamines were converted to the resp. N-(isopropylthio)-N-acylhydroxylamines.
 ST alkanesulfenyl chloride substitution alkoxyphenylurea; phenylurea alkoxy dealkoxylation alkylthiolation; dealkoxylation alkylthiolation alkoxyphenylurea; methoxyamine demethoxylation alkylthiolation; urea phenyl alkylthio; benzenesulfenyl chloride substitution alkoxyphenylurea
 IT Sulfenyl chlorides
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (dealkoxylation-alkylthiolation of alkoxyureas by)

IT Substitution reaction
(dealkoxylation-alkylthiolation, of alkoxyphenylureas by
sulfenyl chlorides)

IT 1496-75-9
RL: RCT (Reactant); RACT (Reactant or reagent)
(dealkoxylation-alkylthiolation of 1-alkoxy-3-phenylureas by)

IT 68692-28-4P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and dealkoxylation-alkylthiolation of)

IT 68692-34-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
(Reactant or reagent)
(preparation and demethoxylation of)

IT 60916-96-3P 68692-38-6P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and demethoxylation-alkylthiolation of)

IT 68692-39-7P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and demethoxylation-benzenethiolation of)

IT 68692-29-5P 68692-31-9P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and thioalkylation of)

IT 68692-30-8P 68692-32-0P 68692-33-1P 68692-35-3P 68692-36-4P
68692-37-5P 68692-40-0P 68692-41-1P 68692-42-2P 68692-43-3P
68692-44-4P 68692-45-5P 68692-46-6P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

IT 594-42-3 931-59-9 937-32-6 19760-04-4
RL: RCT (Reactant); RACT (Reactant or reagent)
(thioalkylation by, of alkoxyphenylureas)

IT 17356-61-5 51458-03-8
RL: RCT (Reactant); RACT (Reactant or reagent)
(thioalkylation of, with sulfenyl chlorides)

IT 52420-54-9
RL: RCT (Reactant); RACT (Reactant or reagent)
(thioethylation of, with ethylsulfenyl chloride)

IT 40750-59-2
RL: RCT (Reactant); RACT (Reactant or reagent)
(N-acylation by N-methoxycarbamate ester)

IT 68692-38-6
RL: RCT (Reactant); RACT (Reactant or reagent)
(N-acylation of aniline derivative by)

IT 79-44-7 7693-46-1
RL: RCT (Reactant); RACT (Reactant or reagent)
(N-acylation of methoxyamine by)

IT 67-62-9
RL: RCT (Reactant); RACT (Reactant or reagent)
(N-acylation reactions with chloroformate ester and carbamoyl chloride
derivative)

IT 31225-17-9
RL: PROC (Process)
(O-tert-butoxylation of)

IT 931-59-9
RL: RCT (Reactant); RACT (Reactant or reagent)
(thioalkylation by, of alkoxyphenylureas)

RN 931-59-9 HCAPLUS

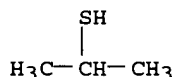
CN Benzenesulfenyl chloride (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)

Ph-S-Cl

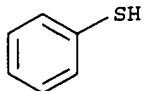
L54 ANSWER 11 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN
AN 1974:551895 HCAPLUS
DN 81:151895

Search done by Ross Schipe

ED Entered STN: 12 May 1984
 TI Novel sulfenylation reagent. Synthesis and reactions of
 N-(arylthio)isatins
 AU Furukawa, Mitsuru; Suda, Tchiaki; Hayashi, Seigoro
 CS Fac. Pharm. Sci., Kumamoto Univ., Kumamoto, Japan
 SO Chemistry Letters (1974), (8), 881-2
 CODEN: CMLTAG; ISSN: 0366-7022
 DT Journal
 LA English
 CC 27-11 (Heterocyclic Compounds (One Hetero Atom))
 OS CASREACT 81:151895
 GI For diagram(s), see printed CA Issue.
 AB N-(Arylthio)isatins (I, R = Ph, 3-MeC6H4, PhCH2, 2-O2NC6H4, 4-ClC6H4) were
 prepared in 73-83% yields by treatment of isatin with RSCl. I were
 efficient sulfur-transfer reagents and react with organometallic compds.,
 thiols and NaCN to give sulfides, disulfides and thiocyanates.
 ST isatin arylthio; sulfenyl chloride isatin reaction; sulfide aryl;
 disulfide aryl; thiocyanate aryl
 IT Sulfenylation
 (reagents, N-(arylthio)isatins as)
 IT 74-96-4 75-33-2 108-40-7 108-86-1 108-98-5
 109-72-8, reactions 591-51-5
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (Grignard reaction with N-(arylthio)isatins)
 IT 139-66-2P 622-38-8P 770-34-3P 882-33-7P 2769-30-4P 3012-37-1P
 5184-47-4P 5285-87-0P 6263-62-3P 13865-48-0P 35379-08-9P
 53888-02-1P 53888-03-2P 53888-04-3P 53888-05-4P 53888-06-5P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 IT 143-33-9
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with N-(arylthio)isatins)
 IT 91-56-5
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with arylsulfenyl chlorides)
 IT 931-59-9 933-01-7 7669-54-7 26826-81-3 38364-78-2
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with isatin)
 IT 75-33-2 108-98-5
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (Grignard reaction with N-(arylthio)isatins)
 RN 75-33-2 HCAPLUS
 CN 2-Propanethiol (8CI, 9CI) (CA INDEX NAME)



RN 108-98-5 HCAPLUS
 CN Benzenethiol (8CI, 9CI) (CA INDEX NAME)



IT 931-59-9
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with isatin)
 RN 931-59-9 HCAPLUS
 CN Benzenesulfenyl chloride (6CI, 7CI, 8CI, 9CI) (CA INDEX NAME)

Ph-S-Cl

L54 ANSWER 12 OF 12 HCAPLUS COPYRIGHT 2005 ACS on STN
 AN 1974:47395 HCAPLUS
 DN 80:47395
 ED Entered STN: 12 May 1984
 TI Derivatives of β -chlorosulphenylcarboxylic acids and their reactions with nucleophilic reagents
 AU Vasil'eva, T. P.; Lin'kova, M. G.; Kil'disheva, O. V.; Knunyants, I. L.
 CS Inst. Elementoorg. Soedin., Moscow, USSR
 SO Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1973), (10), 2379-82
 CODEN: IASKA6; ISSN: 0002-3353
 DT Journal
 LA Russian
 CC 23-12 (Aliphatic Compounds)
 AB AcSH and six ClSCHR1CR2R3COX (R1 = H; R2 = H, Me; R3 = H, Cl; X = OMe, OH, Cl) form at 0° good yields of AcS2CHR1CR2R3COX. A similar reaction with liquid H2S gave four S(SCHR1CHR2COX)2 (R1 = H, Cl; R2 = H, Cl; X = OMe, OH) and the descending order of reactivity with H2S was: ClSCH2CH2CO2Me, ClSCH2CHClCO2Me, ClSCH2CHClCO2H, ClSCHClCH2CO2Me; ClSCHClCH2CO2H failed to react with H2S. The trisulfides decomposed during attempted distillation and formed S and corresponding disulfides. PhMgBr and ClSCH2CHRCO2Me readily gave PhSCH2CHRCO2Me (R = H, Cl).
 ST aliph sulphenyl chloride substitution; hydrogen sulfide substitution reaction; nucleophilic substitution thiolacetic acid
 IT Sulphenyl chlorides
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (aliphatic, substitution reaction of, with nucleophiles)
 IT Nucleophiles
 (hydrogen sulfide and thiolacetic acid, substitution of, with aliphatic sulphenyl chlorides)
 IT Substitution reaction
 (of aliphatic sulphenyl chlorides with nucleophiles)
 IT 108-86-1
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (Grignard reaction of, with aliphatic sulphenyl chlorides)
 IT 20707-94-2P 22198-59-0P 30826-41-6P 32371-96-3P 34036-98-1P
 42801-75-2P 50962-23-7P 50962-24-8P 50962-25-9P 50962-26-0P
 50962-27-1P 50962-28-2P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)
 IT 507-09-5, reactions 7783-06-4, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (substitution reaction of, with aliphatic sulphenyl chlorides)
 IT 41345-79-3
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (substitution reaction of, with hydrogen sulfide)
 IT 41345-74-8 41345-81-7 41345-82-8
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (substitution reaction of, with nucleophiles)
 IT 14274-18-1 14274-19-2 41345-80-6
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (substitution reaction of, with thiolacetic acid)

=> b casre

FILE 'CASREACT' ENTERED AT 10:40:11 ON 23 AUG 2005
 USE IS SUBJECT TO THE TERMS OF YOUR CUSTOMER AGREEMENT
 COPYRIGHT (C) 2005 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is held by the publishers listed in the PUBLISHER (PB) field (available for records published or updated in Chemical Abstracts after December

26, 1996), unless otherwise indicated in the original publications.

FILE CONTENT:1840 - 21 Aug 2005 VOL 143 ISS 8

New CAS Information Use Policies, enter HELP USAGETERMS for details.

```
*****
*
*   CASREACT now has more than 9.2 million reactions
*
*****
```

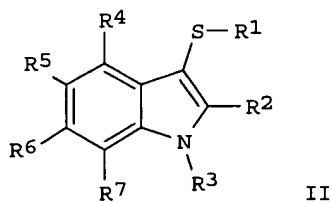
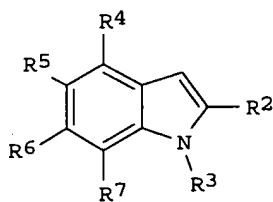
Some CASREACT records are derived from the ZIC/VINITI database (1974-1991) provided by InfoChem, INPI data prior to 1986, and Biotransformations database compiled under the direction of Professor Dr. Klaus Kieslich.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> d bib abs crd 178 tot

L78 ANSWER 1 OF 3 CASREACT COPYRIGHT 2005 ACS on STN
 AN 141:106369 CASREACT
 TI Method for 3-sulfenylation of indole-2-carboxylates by
 chlorination of thiols to sulfenyl chlorides
 IN Wall Hamilton, Harriet; Krasutsky, Alexei P.; Reed, Jessica;
 Schlosser, Kevin
 PA USA
 SO U.S. Pat. Appl. Publ., 13 pp.
 CODEN: USXXCO
 DT Patent
 LA English
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2004133014	A1	20040708	US 2003-631268	20030731
PRAI	US 2002-400092P		20020731		
OS	MARPAT 141:106369				
GI					



AB A highly efficient one-pot procedure for 3-sulfenylation of indole 2-carboxylates is described. Treatment of thiols of formula HSR1 [R1 = C1-6 alkyl, C2-6 alkoxy carbonyl, C3-7 cycloalkyl, C3-7 heterocycloalkyl, C1-6 alkyl-S(O)mRbRc, -C1-6 alkyl-S(O)mNRbRc, C1-6 alkyl-NRbRc, or C1-6 alkyl-CO-NRbRc, aryl, heteroaryl, etc.; m = 1, 2; Ra, Rb, Rc = H, C1-6 alkyl, C3-7 cycloalkyl, C3-6 heterocycloalkyl, or aryl] with N-chlorosuccinimide at -78° in CH2Cl2 affords sulfenyl chlorides of formula R1SCl in situ that readily react with indole 2-carboxylates [I; R2 = CO2H, tetrazolyl, C2-6 alkoxy carbonyl, CONRbRc (Rb, Rc = H, C1-6 alkyl), S(O)mRa, or -S(O)mNRbRc, NRbRc, etc. (wherein m = 1, 2; Ra, Rb, Rc = H, C1-6 alkyl, C3-7 cycloalkyl, C3-6 heterocycloalkyl, or aryl); R3 = H, each optionally substituted alkyl C1-6 or C1-6 alkanoyl; R4-R7 = H, halo, C1-6 alkyl, C1-6 alkoxy, cyano, C3-7

Search done by Ross Schipe

cycloalkyl, C3-7 heterocycloalkyl, C1-6 alkyl-S(O)mRa, -C1-6 -S(O)mNRbRc, C1-6 alkyl-NRbRc, or C1-6 alkyl-CO-NRbRc, C1-6 alkyl-COR1, S(O)mRa, S(O)mNRbRc, NRbRc, CONRbRc, aryl, heteroaryl, etc. (wherein m = 1, 2; Ra, Rb, Rc = H, C1-6 alkyl, C3-7 cycloalkyl, C3-6 heterocycloalkyl, heteroaryl or aryl)] to give 3-thioindoles (II) in high yields. This new method is milder, produces less waste, and is compatible with a wide range of thiol and indole functionality. It is also used for intramol. sulfenylation of N-(2-mercaptoethyl)-1H-indolecarboxamide derivs. to form a indole-fused 1,4-thiaazepane ring. Thus, to a cooled solution of N-chlorosuccinimide (2.74 g, 20.6 mmol) in CH₂Cl₂ (125 mL) at -78°, 3-methoxythiophenol (2.55 mL, 20.6 mmol) was added. The reaction was warmed to 0° over 15 min and a solution of indole-2-carboxylic acid Me ester (3 g, 17.1 mmol) in CH₂Cl₂ (25 mL) was added. The reaction stirred at 0° for 1 h, then concentrated under reduced pressure and the residue was suspended in H₂O and stirred for 30 min to give, after filtration of the solid and recrystn. from EtOAc/hexanes to give 3-[(3-methoxyphenyl)thio]-1H-indole-2-carboxylic acid Me ester (3.22 g, 60%).

NO HIGHLIGHTING INFORMATION PRESENT

L78 ANSWER 2 OF 3 CASREACT COPYRIGHT 2005 ACS on STN
 AN 140:253400 CASREACT
 TI A highly efficient procedure for 3-sulfenylation of indole-2-carboxylates
 AU Schlosser, Kevin M.; Krasutsky, Alexei P.; Hamilton, Harriet W.; Reed, Jessica E.; Sexton, Karen
 CS Department of Chemistry, Pfizer Global Research and Development, Ann Arbor, MI, 48105, USA
 SO Organic Letters (2004), 6(5), 819-821
 CODEN: ORLEF7; ISSN: 1523-7060
 PB American Chemical Society
 DT Journal
 LA English
 AB A highly efficient one-pot procedure for 3-sulfenylation of 2-carboxyindoles is described. Treatment of thiols with N-chlorosuccinimide at -78 °C in CH₂Cl₂ affords sulfenyl chlorides in situ that readily react with 2-carboxyindoles to give 3-thioindoles in high yields. This new method is milder, produces less waste, and is compatible with a wide range of thiol and indole functionality.
 NO HIGHLIGHTING INFORMATION PRESENT
 RE.CNT 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L78 ANSWER 3 OF 3 CASREACT COPYRIGHT 2005 ACS on STN
 AN 128:47859 CASREACT
 TI A ring opening reaction of benzisothiazolones. a new route to unsymmetrical disulfides
 AU Sanchez, Joseph P.
 CS Parke-Davis Pharmaceutical Research, Division of Warner-Lambert Company, Ann Arbor, MI, 48105, USA
 SO Journal of Heterocyclic Chemistry (1997), 34(5), 1463-1467
 CODEN: JHTCAD; ISSN: 0022-152X
 PB HeteroCorporation
 DT Journal
 LA English
 AB A series of unsym. disulfides has been prepared by employing a reaction involving a ring opening, nucleophilic attack of a thiol on a 1,2-benzisothiazol-3-one. The benzisothiazolones were in turn prepared by an intramol. ring closure of an amide on a sulfenyl thiocarbonate. The sulfenyl esters were synthesized as intermediates for preparing mixed-disulfides, but the benzisothiazolone ring closure occurred spontaneously. It was initially thought that the mixed-disulfides were being formed from the sulfenyl ester, but the isolation and stepwise reaction of the benzisothiazolones provided

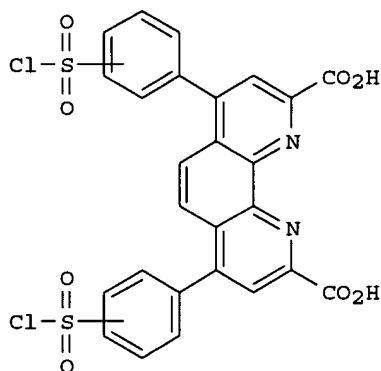
proof for the reaction mechanism.

NO HIGHLIGHTING INFORMATION PRESENT

RE.CNT 25 THERE ARE 25 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> d bib abs crd 177 tot

L77 ANSWER 1 OF 17 CASREACT COPYRIGHT 2005 ACS on STN
AN 138:205029 CASREACT
TI Synthesis and characterization of time resolved fluorescence immunoassay chelate reagent 4,7-bis(chlorosulfophenyl)-1,10-phenanthroline-2,9-dicarboxylic acid (BCPDA). (II)
AU Pan, Li-hua; Gao, Min; Lin, Min; Ding, Chun-li; Sun, Wen-wei; Zhao, Jie
CS Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, Peop. Rep. China
SO Guangpuxue Yu Guangpu Fenxi (2002), 22(4), 573-576
CODEN: GYG FED; ISSN: 1000-0593
PB Beijing Daxue Chubanshe
DT Journal
LA Chinese
GI



AB Title compound I, a fluorescent labeling agent, was synthesized from 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, via chlorization the di-Me group, hydrolyzation to the ester, forming the disodium salt, after acidifying, giving the corresponding dicarboxylic acid, further sulfonation, got the product with high yield. The structure and purity of product was characterized by the m.p., IR, 1H NMR, UV spectrum, element anal..

RX(15) OF 15 - REACTION DIAGRAM NOT AVAILABLE

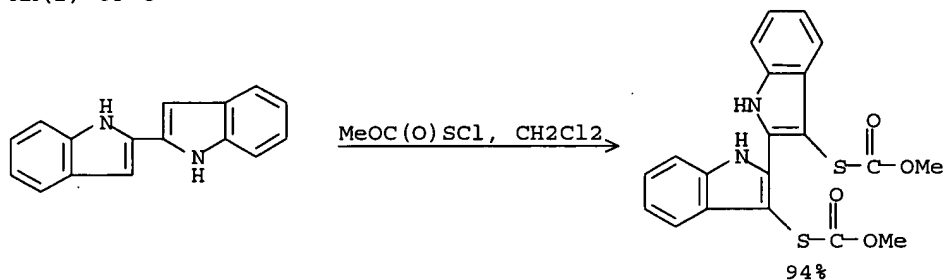
L77 ANSWER 2 OF 17 CASREACT COPYRIGHT 2005 ACS on STN
AN 137:201292 CASREACT
TI Synthetic, spectroscopic, and X-ray crystallographic studies of [1,2,7,8]tetrathiacyclododecino[4,3-b:5,6-b':10,9-b'':11,12-b''']tetraindoles
AU Janosik, Tomasz; Bergman, Jan; Romero, Ivan; Stensland, Birgitta; Stalhandske, Claes; Marques, M. Manuel B.; Santos, Maria M. M.; Lobo, Ana M.; Prabhakar, Sundaresan; Duarte, M. Filomena; Florencio, M. Helena
CS Unit for Organic Chemistry, CNT, Department of Biosciences at Novum, Karolinska Institute, Huddinge, 141 57, Swed.
SO European Journal of Organic Chemistry (2002), (8), 1392-1396
CODEN: EJOCFK; ISSN: 1434-193X

PB Wiley-VCH Verlag GmbH
 DT Journal
 LA English
 GI

* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB Two conformationally different [1,2,7,8]tetrathiacyclododecino[4,3-b:5,6-b':10,9-b'':11,12-b''']tetraindoles (I) and (II) were isolated in good yields, and the existence of a third conformer in solution was demonstrated by mass spectrometry and ¹H NMR spectroscopy. The interconversions of the tetraindoles was studied. The conformation of II was confirmed by x-ray crystallog., while the conformations of I and II were assigned on the basis of spectroscopic data, and were also supported by mol. modeling studies. In addition, the elusive [1,2]dithiino[4,3-b:5,6-b']diindole-N,N-dimethylacetamide was isolated and the structure was proven by x-ray crystallog.

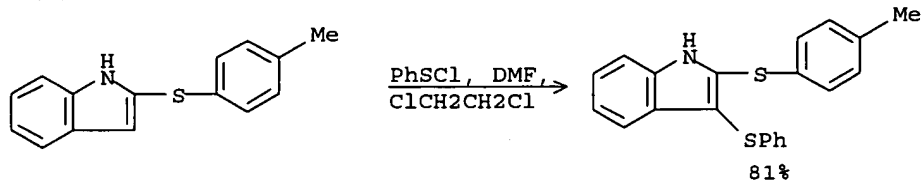
RX(2) OF 8



RE.CNT 22 THERE ARE 22 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

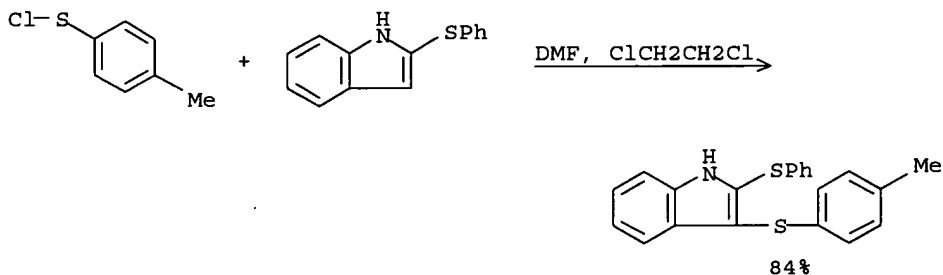
L77 ANSWER 3 OF 17 CASREACT COPYRIGHT 2005 ACS on STN
 AN 136:401369 CASREACT
 TI Mechanism of the Second Sulfenylation of Indole
 AU Hamel, Pierre
 CS The Merck Frosst Centre for Therapeutic Research, Pointe-Claire-Dorval, QC, H9R 4P8, Can.
 SO Journal of Organic Chemistry (2002), 67(9), 2854-2858
 CODEN: JOCEAH; ISSN: 0022-3263
 PB American Chemical Society
 DT Journal
 LA English
 AB Sulfenylation of indole using a sulfenyl chloride occurs initially at the 3-position of the ring, leading to a 3-indolyl sulfide. When an excess of sulfenyl chloride is used, a second sulfide group is introduced at the 2-position, and an indolyl 2,3-bis-sulfide results. We have demonstrated that this second sulfenylation occurs not by direct introduction of the second sulfide at the 2-position but via initial formation of an indolenium 3,3-bis-sulfide intermediate, followed by migration of one of the sulfide groups to the 2-position. This was achieved by the isolation of two examples of 3H-indole 3,3-bis-sulfides and by subsequent demonstration that they rearrange to the indolyl 2,3-bis-sulfides by treatment with sulfenyl halides.

RX(3) OF 11



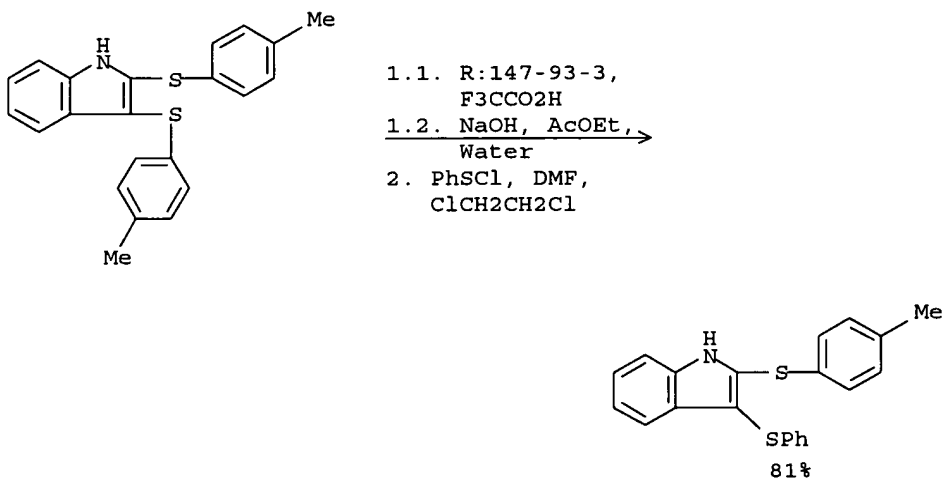
NOTE: in-situ generated reactant

RX(4) OF 11



NOTE: in-situ generated reactant

RX(10) OF 11 - 2 STEPS



NOTE: 2) in-situ generated reactant

RE.CNT 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L77 ANSWER 4 OF 17 CASREACT COPYRIGHT 2005 ACS on STN
AN 136:369255 CASREACT
TI Reactions of 1,3,3,3-tetrafluoro-2-methoxycarbonylpropenylsulfenyl chloride with aromatic and heterocyclic compounds
AU Kovregin, A. N.; Sizov, A. Yu.; Ermolov, A. F.
CS Military University of Radiational, Chemical, Defence, Moscow, 107005, Russia
SO Russian Chemical Bulletin (Translation of Izvestiya Akademii Nauk, Seriya Khimicheskaya) (2001), 50(7), 1255-1258

Search done by Ross Schipe

CODEN: RCBUEY; ISSN: 1066-5285

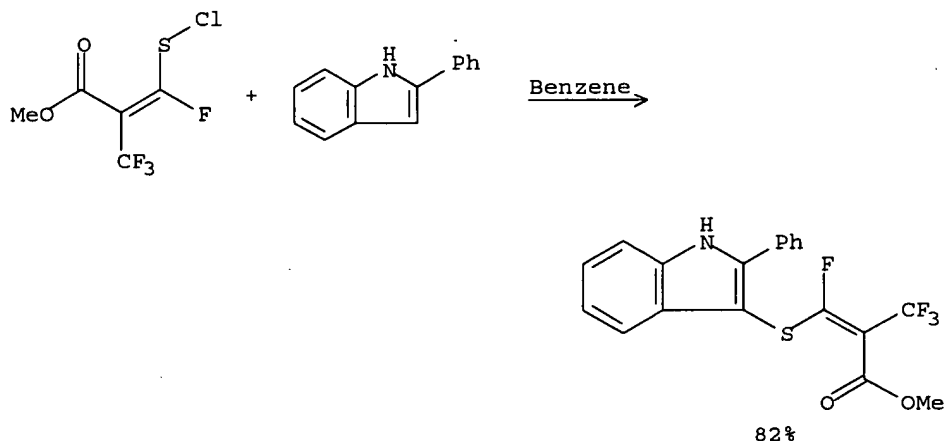
PB Kluwer Academic/Consultants Bureau

DT Journal

LA English

AB 1,3,3,3-Tetrafluoro-2-methoxycarbonylpropenylsulfenyl chloride [i.e., 3-(chlorothio)-3-fluoro-2-(trifluoromethyl)-2-propenoic acid Me ester (I)] readily reacts with activated aromatic and heterocyclic compds. to form C-sulfenylation products as E isomers. In some cases, the reaction of I with phenolic compds. was accompanied by cyclization giving rise to fused 2-(2,2,2-trifluoro-1-methoxycarbonylethylidene)-1,3-oxathioles.

RX(4) OF 19



NOTE: stereoselective

RE.CNT 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L77 ANSWER 5 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 112:76699 CASREACT

TI Synthesis of 3-(alkyl and aryl)thio-2-isocephems

AU Aszodi, Jozsef; Chantot, Jean Francois; Collard, Jeannine; Teutsch, Georges

CS Cent. Rech. Roussel Uclaf, Romainville, 93230, Fr.

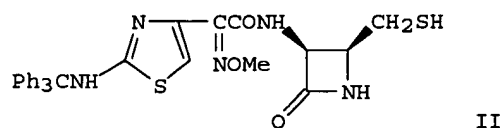
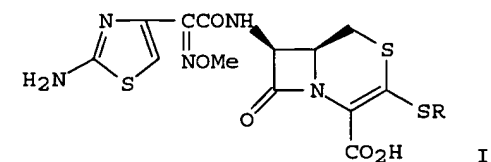
SO Heterocycles (1989), 28(2), 1061-76

CODEN: HTCYAM; ISSN: 0385-5414

DT Journal

LA English

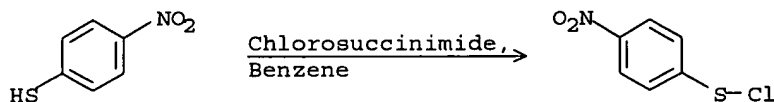
GI



Search done by Ross Schipe

AB Isocephems I (R = Ph, 4-MeOC₆H₄, 4-O₂NC₆H₄, 1-methyl-5-tetrazolyl, 5-methyl-1,3,4-thiadiazol-2-yl, CH₂CO₂H, CH₂CH₂NH₂, CH₂C₆H₄NO₂-4) were prepared from the mercaptomethylazetidinone II and RSCHClCOCO₂CMe₃, prepared from RSU and N₂CHCOCO₂CMe₃. Acid-catalyzed decarboxylation was a side-reaction in the deblocking step. Some I were more active against Staphylococci than cefotaxime, but I had poor activity against gram-neg. organisms.

RX(3) OF 85



L77 ANSWER 6 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 111:173585 CASREACT

TI Thioformyl cyanide. Gas-phase synthesis and millimeter wave spectrum

AU Bogey, Marcel; Demuyne, Claire; Destombes, Jean Luc; Gaumont, Annie; Denis, Jean Marc; Vallee, Yolande; Ripoll, Jean Louis

CS Lab. Spectrosc. Hertzienne, Univ. Lille I, Villeneuve d'Ascq, 59655, Fr.

SO Journal of the American Chemical Society (1989), 111(19), 7399-402

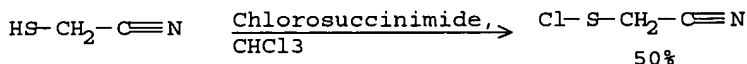
CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

AB The monomeric thioformyl cyanide HCSCN has been generated in the gas phase, either by flash-thermolytic retro-ene reaction of allylcyanomethyl sulfide or by vacuum gas-solid dehydrochlorination of cyanomethylsulfenyl chloride over potassium carbonate. An investigation by millimeter wave spectroscopy led to the unambiguous identification, mol. consts., and lifetime of HCSCN.

RX(5) OF 8



L77 ANSWER 7 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 111:57025 CASREACT

TI Reactions of Wittig reagents with episulfides or elemental sulfur

AU Okuma, Kentaro; Tachibana, Yuji; Sakata, Junichi; Komiya, Takashi; Kaneko, Isao; Komiya, Yasuo; Yamasaki, Yusuke; Yamamoto, Shinichi; Ohta, Hiroshi

CS Fac. Sci., Fukuoka Univ., Fukuoka, 814-01, Japan

SO Bulletin of the Chemical Society of Japan (1988), 61(12), 4323-7

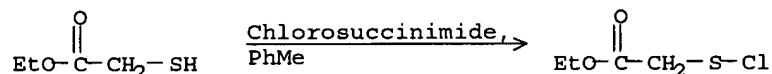
CODEN: BCSJA8; ISSN: 0009-2673

DT Journal

LA English

AB The reactions of Wittig reagents with episulfides gave sym. olefins and Ph₃PS in moderate yields. The same olefins were obtained by reactions of Wittig reagents with elemental S. These reactions proceed through thiocarbonyl intermediates, the existence of which was confirmed by Diels-Alder reactions with dienes.

RX(3) OF 20



L77 ANSWER 8 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 109:230907 CASREACT

TI Preparation of carboxythioamides by the reaction of thioaldehydes with secondary amines

AU Okuma, Kentaro; Honda, Takumi; Ohta, Hiroshi

CS Fac. Sci., Fukuoka Univ., Fukuoka, 814-01, Japan

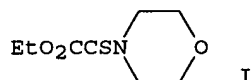
SO Fukuoka Daigaku Rigaku Shuho (1987), 17(2), 41-4

CODEN: FDRSDG; ISSN: 0386-118X

DT Journal

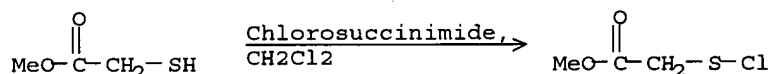
LA English

GI



AB The reactions of thioaldehydes with amines were carried out. When carboxymethanesulfonyl chlorides were treated with secondary amines in the presence of Et₃N, carboxythioamides, e.g., I, were obtained. Ordinary sulfonylchlorides reacted with secondary amines to give corresponding sulfenamides.

RX(12) OF 14



L77 ANSWER 9 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 106:49947 CASREACT

TI Electron-transfer processes: sulfonylation of electron-rich systems by diaryl disulfides and aryl thiosulfonates

AU Berti, Corrado; Colonna, Martino; Poloni, Marino

CS Fac. Ing., Univ. Bologna, Bologna, I-40136, Italy

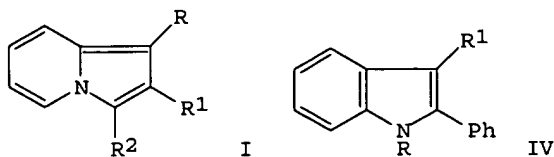
SO Gazzetta Chimica Italiana (1986), 116(4), 181-4

CODEN: GCITA9; ISSN: 0016-5603

DT Journal

LA English

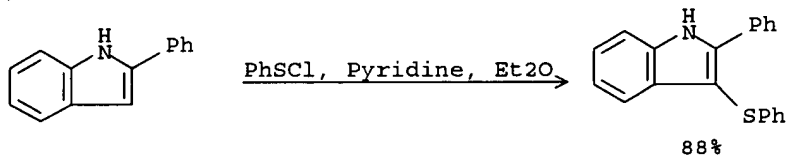
GI



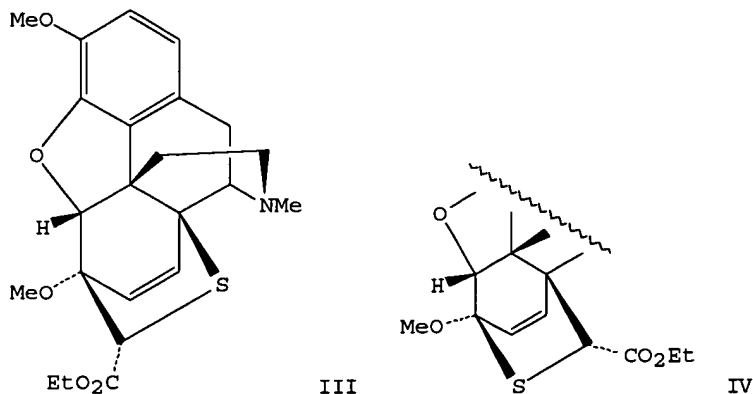
AB Sulfonylation of indolizine I (R = Me, R₁ = Ph, R₂ = H) with PhSSPh (II) in refluxing EtOH gave I (R₂ = SPh). Dibenzothiazol-2-yl disulfide (III),

a compound with a low S-S bond energy, reacted with I (R = Me, R1 = Ph, R2 = H; R = H, R1 = Ph, R2 = Me) at room temperature giving I (R = Me, R1 = Ph, R2 = benzothiazol-2-ylthio; R = benzothiazol-2-ylthio, R1 = Ph, R2 = Me) in 66-92% yields. Indoles IV (R = H, Me; R1 = H), which have a higher oxidation potential than indolizines, reacted with II only on irradiation. The sulfenylation of IV can be easily obtained either by activation with AgNO₃ or using III. PhSSO₂C₆H₄Cl-4 sulfenylated I (R = Me, R1 = Ph, R2 = H) and IV at room temperature. All these reactions are discussed in terms of electron-transfer processes.

RX(10) OF 15

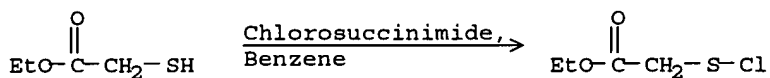


L77 ANSWER 10 OF 17 CASREACT COPYRIGHT 2005 ACS on STN
 AN 104:5547 CASREACT
 TI Ethyl and methyl thioacetates, dienophilic thioaldehydes formed from sulfenyl chlorides by 1,2-elimination
 AU Bladon, Christine M.; Ferguson, Irene E. G.; Kirby, Gordon W.; Lochead, Alistair W.; McDougall, Duncan C.
 CS Dep. Chem., Univ. Glasgow, Glasgow, G12 8QQ, UK
 SO Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999) (1985), (7), 1541-5
 CODEN: JCPRB4; ISSN: 0300-922X
 DT Journal
 LA English
 GI

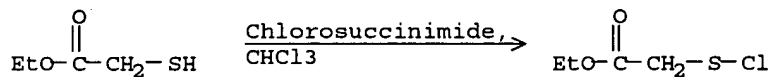


AB Treatment of RO₂CCH₂SCl (I; R = Me, Et) with Et₃N at room temperature gave the corresponding RO₂CCHS (II). Generation of transient II (R = Et) in the presence of conjugated dienes gave the corresponding cycloadducts. E.g., treatment of I (R = Et) with Et₃N in C₆H₆-MeOH containing thebaine at room temperature gave 67% cycloadduct III, which isomerized at 111° to the more stable adduct IV by dissociation and recombination. Cycloadducts of II (R = Et) and anthracene or 9,10-dimethylantracene similarly dissociated at 111°, providing a clean and convenient source of II (R = Et).

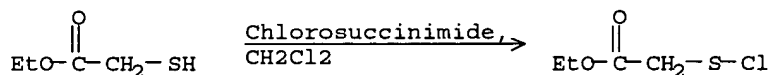
RX(1) OF 58



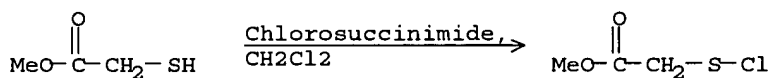
RX(2) OF 58



RX(3) OF 58



RX(4) OF 58



L77 ANSWER 11 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 103:123385 CASREACT

TI Thiopyranothiopyran chemistry. 5. Synthesis of dibenzo[b,g]thiopyrano[3,2-b]thiopyran-6,12-dione (thioepindolidione)

AU Chen, Chin H.; Fox, John L.

CS Res. Lab., Eastman Kodak Co., Rochester, NY, 14650, USA

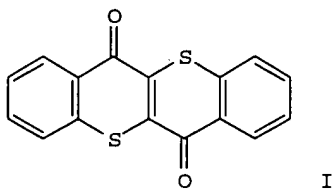
SO Journal of Organic Chemistry (1985), 50(19), 3592-5

CODEN: JOCEAH; ISSN: 0022-3263

DT Journal

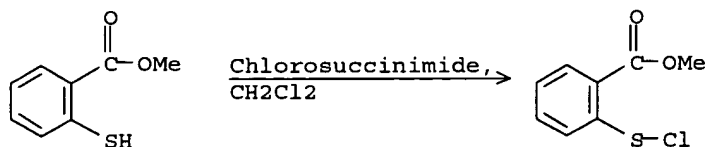
LA English

GI



AB Thioepindolidione (I), a derivative of a thiopyrano[3,2-b]thiopyran, was synthesized along with trans-thioindigo from thiochroman-4-one. The absorption and fluorescence characteristics and chromogenic properties of I are compared with those of thioindigo and epindolidione.

RX(2) OF 28



L77 ANSWER 12 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 103:37318 CASREACT

TI Methanesulfonylation of 2,3-dialkylindoles: synthesis and reactions of 3-methylthioindolenines

AU Friesen, Richard W.; Vice, Susan F.; Findlay, C. Edward; Dmitrienko, Gary I.

CS Guelph-Waterloo Cent. Grad. Work Chem., Univ. Waterloo, Waterloo, ON, N2L 3G1, Can.

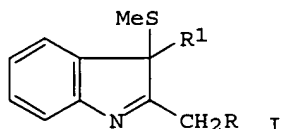
SO Tetrahedron Letters (1985), 26(2), 161-4

CODEN: TELEAY; ISSN: 0040-4039

DT Journal

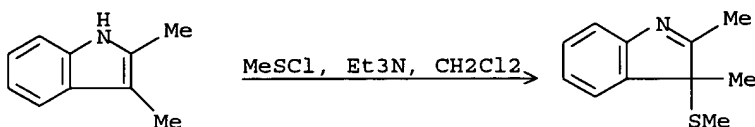
LA English

GI

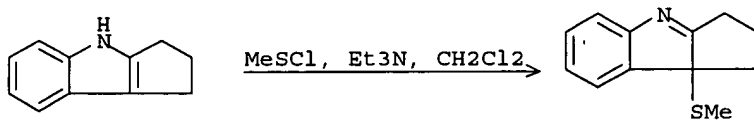


AB 3-Methylthioindolenines I [$\text{R} = \text{H}$, $\text{R}^1 = \text{Me}$, $\text{RR}^1 = (\text{CH}_2)_2$, $(\text{CH}_2)_3$], readily prepared from 2,3-dialkylindoles and MeSCl , are heat and acid labile, yielding the parent indole and MeSSMe as the major decomposition products, and are readily reduced to the parent indoles with mercaptoacetic acid.

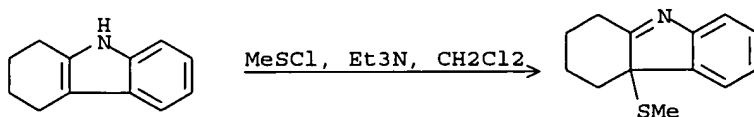
RX(8) OF 12



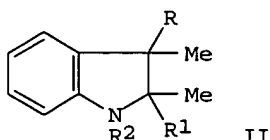
RX(9) OF 12



RX(10) OF 12

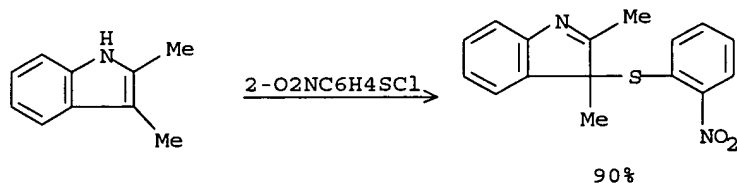


L77 ANSWER 13 OF 17 CASREACT COPYRIGHT 2005 ACS on STN
 AN 97:23571 CASREACT
 TI Arylsulfonylation of 2,3-dialkylindoles. Preparation of
 3-arylthioindolenines and thermal conversion to an N-sulfonylindole
 AU Dmitrienko, Gary I.; Friesen, Richard W.; Carson, Loraine; Vice, Susan F.
 CS Guelph-Waterloo Cent. Grad. Work Chem., Univ. Waterloo, Waterloo, N2L 3G1,
 Can.
 SO Tetrahedron Letters (1982), 23(8), 821-4
 CODEN: TELEAY; ISSN: 0040-4039
 DT Journal
 LA English
 GI

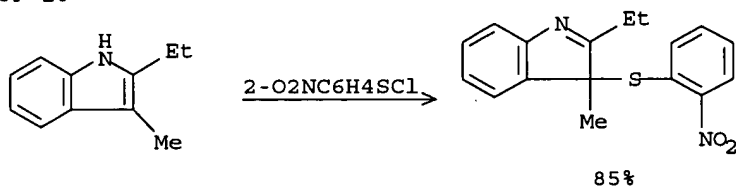


AB Reaction of ClSC₆H₄NO₂-o (I) with 2,3-dialkylindoles gave
 3-(o-nitrophenylsulfonyl)-2,3-dialkylindolenines which underwent thermal
 rearrangement to give N-(o-nitrophenylsulfonyl)indoles. Thus, I reacted
 with 2,3-dimethylindole in the presence of Et₃N to give 90% indole II (R =
 SC₆H₄NO₂-o, R₁R₂ = bond) (III). Heating III at 95° for 15 min gave
 14% II (RR₁ = bond, R₂ = SC₆H₄NO₂-o).

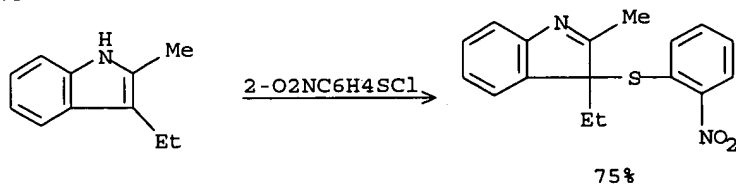
RX(2) OF 10



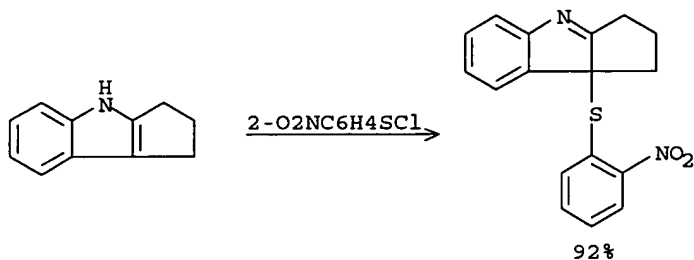
RX(3) OF 10



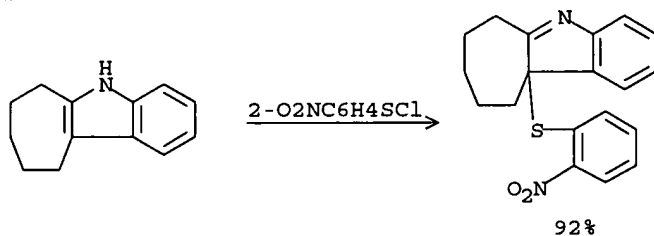
RX(4) OF 10



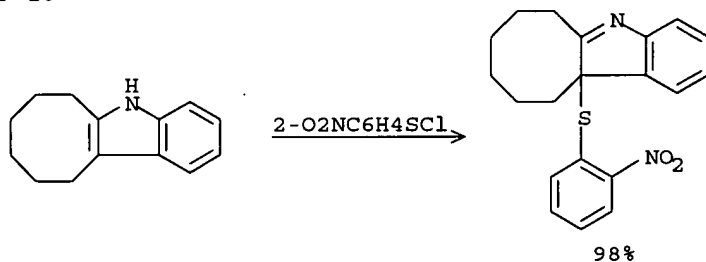
RX(5) OF 10



RX(6) OF 10



RX(7) OF 10



L77 ANSWER 14 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 95:187068 CASREACT

TI Antidiabetic pyrrolicarboxylic acids

IN Holland, Gerald F.

PA Pfizer Inc., USA

SO U.S., 28 pp.

CODEN: USXXAM

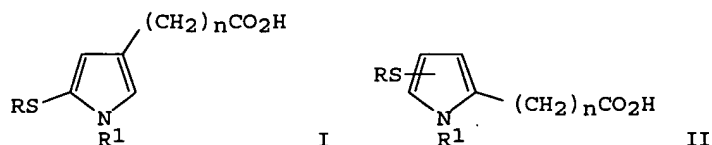
DT Patent

LA English

FAN.CNT 1

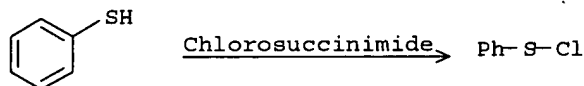
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4282242	A	19810804	US 1980-128119	19800307
	US 4351843	A	19820928	US 1981-256933	19810423
	US 4511575	A	19850416	US 1982-406306	19820809
	US 4511576	A	19850416	US 1982-406921	19820810
PRAI	US 1980-128119		19800307		
	US 1981-256933		19810423		

GI



AB Pyrrolecaboxylates I and II (R = alkyl, CH₂Ph, optionally substituted Ph; R₁ = H, Me, Et; n = 0, 1) were prepared. Thus CH₂:CHCO₂Me was treated with 4-MeC₆H₄SO₂CH₂NC to give Me 3-pyrrolecaboxylate which was treated with PhSCl and saponified to give I (R = Ph, R₁ = H, n = 0).

RX(1) OF 39



L77 ANSWER 15 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 93:7609 CASREACT

TI Synthesis of aliphatic sulfenyl halides containing ester groups

AU Seliger, Hartmut; Goertz, Hans Helmut

CS Sekt. Polym., Univ. Ulm, Ulm, D-7900, Fed. Rep. Ger.

SO Synthetic Communications (1980), 10(3), 175-82

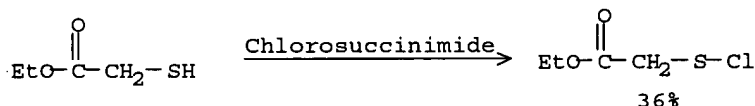
CODEN: SYNCAV; ISSN: 0039-7911

DT Journal

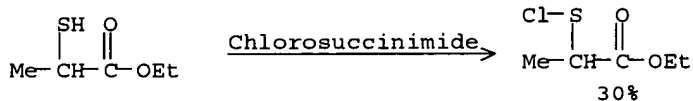
LA English

AB Aliphatic sulfenyl halides RCO₂CH₂CH₂SR₁ (I, R = H, Me, Et, F₃C; R₁ = Cl, Br), AcOCHR₂CHR₃SR₁ (II, R₁ = Cl, Br; R₂ = Me, Et, R₃ = H; R₂R₃ = (CH₂)₄], and EtO₂C(CH₂)_nCHR₄SR₁ (III, R₁ = Cl, Br; n = 0, R₄ = H, Me; n = 1, R₄ = CO₂Et) were prepared. I-III (R₁ = H) were treated with N-chlorosuccinimide to give 31% to 72% I-III (R₁ = Cl). I-III (R₁ = Br) were prepared similarly, but decomposed on heating to the corresponding disulfides with elimination of Br.

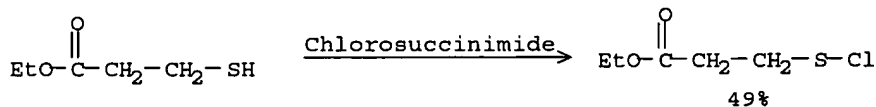
RX(14) OF 67



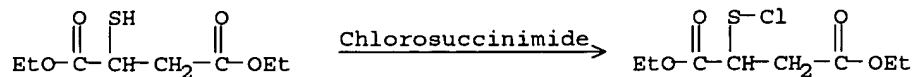
RX(15) OF 67



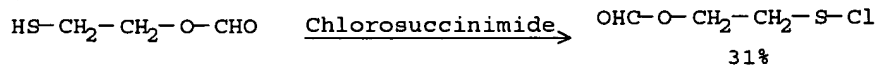
RX(16) OF 67



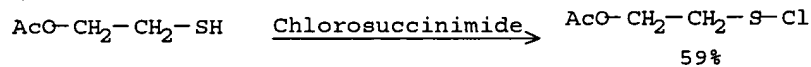
RX(17) OF 67



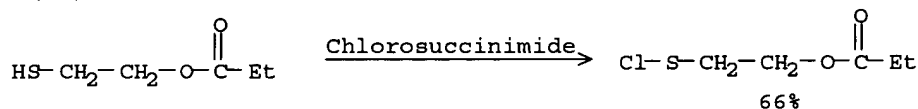
RX(18) OF 67



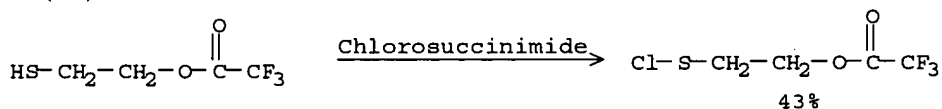
RX(19) OF 67



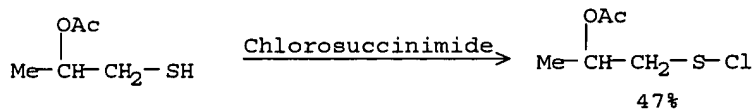
RX(20) OF 67



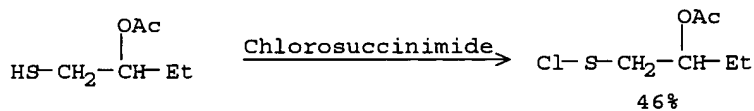
RX(21) OF 67



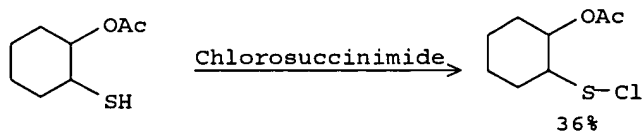
RX(22) OF 67



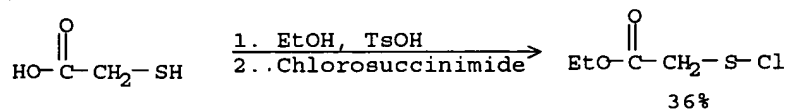
RX(23) OF 67



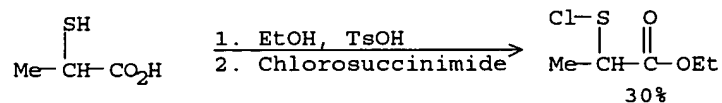
RX(24) OF 67



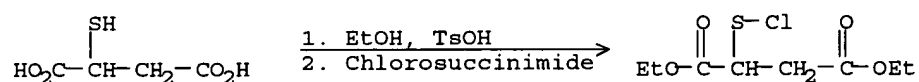
RX(37) OF 67 - 2 STEPS



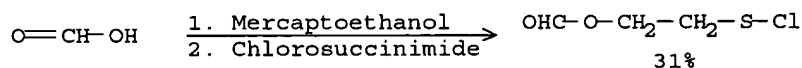
RX(39) OF 67 - 2 STEPS



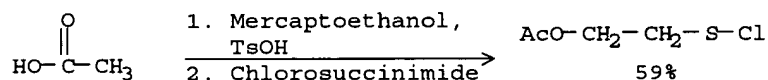
RX(41) OF 67 - 2 STEPS



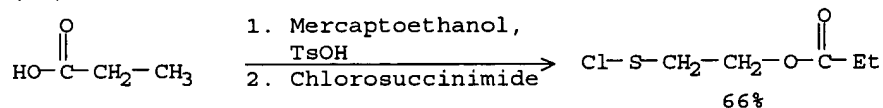
RX(43) OF 67 - 2 STEPS



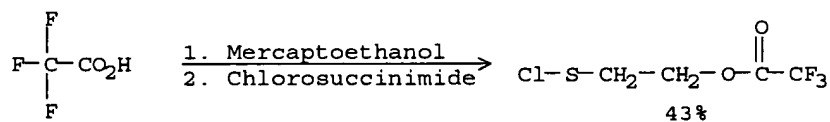
RX(45) OF 67 - 2 STEPS



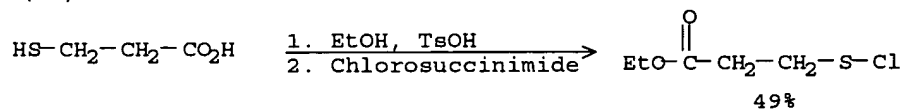
RX(47) OF 67 - 2 STEPS



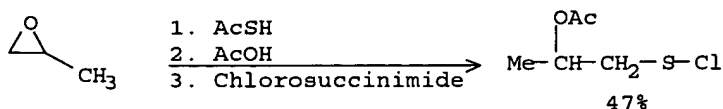
RX(49) OF 67 - 2 STEPS



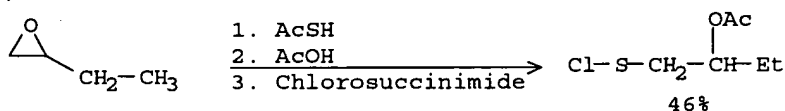
RX(60) OF 67 - 2 STEPS



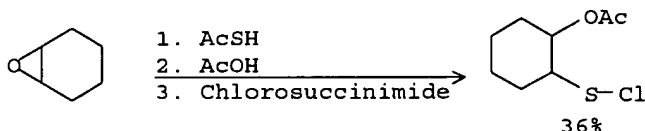
RX(62) OF 67 - 3 STEPS



RX(64) OF 67 - 3 STEPS



RX(66) OF 67 - 3 STEPS



L77 ANSWER 16 OF 17 CASREACT COPYRIGHT 2005 ACS on STN

AN 67:63971 CASREACT

TI A search for agents protecting against irradiation IX. Synthesis of some asymmetric disulfides

AU Tulecki, Jerzy; Dabrowski, Jerzy; Kalinowska-Torz, Jadwiga

CS Katedra Tech. Chem. Srodkow Leczniczych, Akad. Med., Poznan, Pol.

SO Dissertationes Pharmaceuticae et Pharmacologicae (1966), 18(5), 473-8

CODEN: DPHFAK; ISSN: 0012-3870

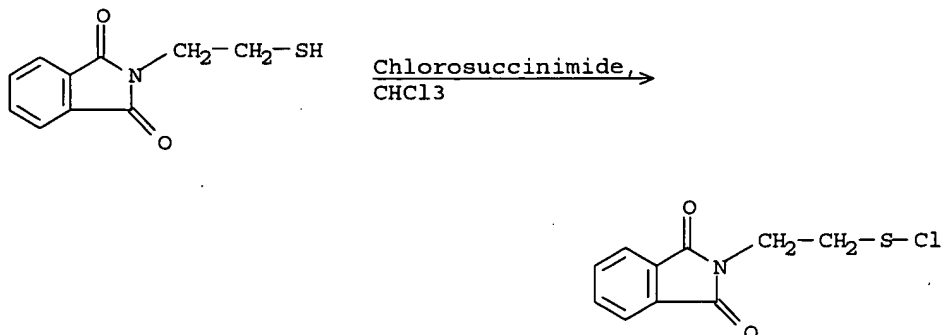
DT Journal

LA Polish

GI For diagram(s), see printed CA Issue.

AB Bromoethylphthalimide (74.2 g.) and 22.3 g. thiourea in 240 ml. 90% EtOH was refluxed 4 hrs., the dry residue dissolved in 300 ml. H₂O and treated with 0.5 g. Na₂SO₃ and then with 16.5 g. KOH in 100 ml. H₂O, and the mixture heated 30 min. on a steam bath to give 50.4 g. 2-mercaptoethylphthalimide (I), m. 74-5.5°; 2,4-dinitrophenyl derivative m. 186-7°. I (2.2 g.) in 70 ml. CHCl₃ treated with 1.4 g. N-chlorosuccinimide (26% Cl+) gave, after 10 min., phthalimide-N-ethylsulfenyl chloride (II), which when mixed with 1.6 g. thiosalicylic acid in 130 ml. Et₂O gave 77% o-carboxyphenyl 2-phthalimidoethyl disulfide (III), m. 208-12° and 219-21°. II, obtained from 4.8 g. I, in 70 ml. CHCl₃ was kept with 3.8 g. 2-mercaptothiazole in 200 ml. CHCl₃ 10 min. and refluxed 10 min. to give 69.5% 2-benzothiazolyl 2-phthalimidoethyl disulfide (IV), m. 133-4°. Similarly, 68.3% 2-furfuryl 2-phthalimidoethyl disulfide, m. 95-5.5°, was obtained from II and furfuryl mercaptan. Thiosalicylic acid (2.7 g.) in 30 ml. CHCl₃ added dropwise to 2.5 g. N-chlorosuccinimide in 60 ml. CHCl₃ gave the sulfenyl chloride, which treated with 3-phenyl-propyl mercaptan in 30 ml. CHCl₃ at room temperature and kept 20 min. yielded 62% o-carboxyphenyl 3-phenylpropyl disulfide (V), m. 100-100.5°. Cf. CA 67: 53825n.

RX(2) OF 2

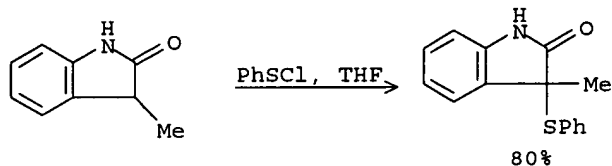


NOTE: Classification: Chlorination; # Conditions: NCS CHCl₃; 10mn; #
 Comments: also C.A., 67, 6002 (1967)

L77 ANSWER 17 OF 17 CASREACT COPYRIGHT 2005 ACS on STN
 AN 63:38959 CASREACT
 TI Indoles for comparison with amanita poisons. V. Thio ether syntheses in the oxindole, indoline, and indole series
 AU Wieland, Theodor; Grimm, Dieter
 CS Univ. Frankfurt, Germany
 SO Chemische Berichte (1965), 98(6), 1727-35
 CODEN: CHBEAM; ISSN: 0009-2940
 DT Journal
 LA German
 AB cf. CA 58, 11310c. The thioether grouping was introduced into 3-substituted oxindoles via the 3-Br derivative with mercaptides or by direct substitution of H with sulphenyl chlorides. The resulting oxindole 3-thio ethers could not be reduced to the corresponding indolines since the Scontg. substituent was cleaved off by the LiAlH₄. The introduction of thio ether groups into the 2-position of 3-substituted 6-methoxyindoles was achieved with sulphenyl chlorides; the resulting products showed uv spectra very similar to that of amanitine. 3-Methyloxindole (I) (7.3 g.) in 200 cc. CCl₄ treated dropwise with 8 g. Br in 400 cc. CCl₄ yielded 10 g. 3-Br derivative (II) of I, m. 220-2° (decomposition). II (5.65 g.) in 40 cc. dry tetrahydrofuran refluxed 2 hrs. with 2.10 g. EtSNa and kept overnight gave 4.0 g. 3-EtS derivative (III) of I, m. 74° (repptd. from EtOH with H₂O). III (2.07g.) in 30 cc. dry dioxane heated 3 hrs. with 0.37 g. LiAlH₄ in 10 cc. dry Et₂O gave skatole, m. 86-8° (aqueous MeOH). PhSH (d. 1.078) (1.1 g.) added with cooling to 1.34 g. N-chlorosuccinimide in 2 cc. dry CHCl₃ and 3 cc. dry tetrahydrofuran gave a solution of PhSCL (IV). The PhSCL solution and 1.47 g. I in tetrahydrofuran kept 1 hr. at room temperature yielded 2.1 g. 3-PhS derivative of I, m. 163° (aqueous MeOH). IV from 1.02 g. PhSH and 1.35 g. N-chlorosuccinimide treated 2 hrs. at room temperature with 0.7 g. 1-methyloxindole (V) gave 1.0 g. 3-PhS derivative of V, m. 118° (aqueous MeOH). 5-Ethoxy-1,3-dimethyloxindole (VI) (2.0 g.) in 10 cc. tetrahydrofuran treated 2 hrs. with IV from 1.02 g. PhSH and 1.35 g. N-chlorosuccinimide gave 2.0 g. 3-PhS derivative of VI, m. 60° (aqueous MeOH). Trimeric 3,3-dimethylindolenine (4.34 g.) in 60 cc. C₆H₆ and 3.44 g. BzCl treated 2 hrs. at room temperature with 0.69 g. Na in 15 cc. EtSH yielded 7.0 g. 2-ethylthio-3,3-dimethyl-1-benzoylindoline, b0.01 165-8°. AcEtCHCO₂Et (40 g.) dissolved at -15° in 190 cc. 20% aqueous NaOH and 190 cc. EtOH, treated at -10° with diazotized 30.9 g. m-MeOC₆H₄NH₂, and stirred 0.5 hr. at -4° and a 60-g. portion of the resulting 65 g. oily hydrazone refluxed 45 min. with 300 cc. absolute EtOH and 45 cc. concentrated H₂SO₄ yielded 21 g. 2-carbethoxy-3-methyl-6-methoxyindole (VII), m. 122° (petr. ether). VII (15 g.), 187 cc. 10% aqueous NaOH, and 50 cc. EtOH refluxed 5 hrs. yielded 14 g. 2-CO₂H analog (VIII) of VII, m. 202° (aqueous EtOH). VIII heated 0.5 hr. at

220° gave about 70% 3-methyl-6-methoxyindole (IX), m. 127° (aqueous MeOH). IX (1.92 g.) in 20 cc. dry Et2O treated dropwise with stirring under N at 0° with 1.2 g. EtSCl in 20 cc. CHCl3 and kept 2 hrs. at 0° and 2 hrs. at room temperature yielded 1.42 g. X (R = Me, R' = Et) (XI), m. 138° (sublimed at 130-40°/0.005 mm.). The S-Cl derivative from 2.55 g. N-carbobenzyloxycysteine (XII) and 1.35 g. N-chlorosuccinimide (XIII) treated with 1.61 g. IX yielded 2.5 g. X [R = Me, R' = PhCH2O2CNHCH(CO2H)CH2], decomposed from 90° (Et2O-petr. ether). Diethyl acetamido(6-methoxy-3-indolylmethyl)malonate (0.752 g.), m. 145°, treated with the S-Cl derivative from 0.51 g. XII and 0.27 g. XIII in 6 cc. dry CHCl3 and 4 cc. dry tetrahydrofuran yielded 1.0 g. X [R = AcNHC(CO2Et)2CH2, R' = PhCH2O2CNHCH(CO2H)CH2] (XIV), m. 103° (Et2O-petr. ether). The uv spectra of IX, XI, VIII, and XIV are recorded.

RX(1) OF 2



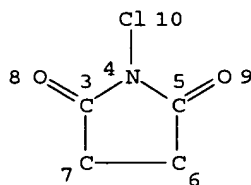
=> d que sta 157

L55 STR

RRT

RRT

PRO

S---H
1 2S---X
11 12

NODE ATTRIBUTES:

DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED

NUMBER OF NODES IS 12

STEREO ATTRIBUTES: NONE

L57 12 SEA FILE=CASREACT SSS FUL L55 (36 REACTIONS)

100.0% DONE 259 VERIFIED

36 HIT RXNS

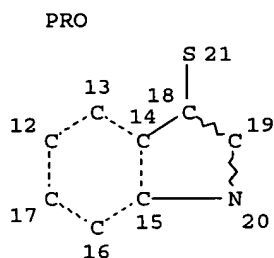
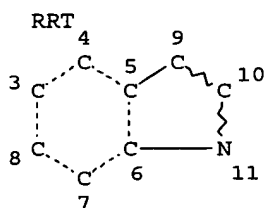
12 DOCS

SEARCH TIME: 00.00.01

=> d que sta 172

L70 STR

RRT
S—X
1 2



NODE ATTRIBUTES:

CONNECT IS E2 RC AT 1
CONNECT IS E3 RC AT 10
CONNECT IS E3 RC AT 19
CONNECT IS E2 RC AT 21
DEFAULT MLEVEL IS ATOM
DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:

RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 21

STEREO ATTRIBUTES: NONE

L72 7 SEA FILE=CASREACT SSS FUL L70 (16 REACTIONS)

100.0% DONE 771 VERIFIED 16 HIT RXNS
SEARCH TIME: 00.00.02

7 DOCS

=> b home

FILE 'HOME' ENTERED AT 10:41:58 ON 23 AUG 2005

=>